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THE UNIVERSITY OF ALBERTA

CHEMISTRY OF THE CARBONYL(η-CYCLOPENTADIENYL)NITROSYLRHENIUM GROUP

by

© JAMES RONALD SWEET

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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DEPARTMENT OF CHEMISTRY

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled CHEMISTRY OF THE CARBONYL(η-CYCLOPENTADIENYL)NITROSYLRHENIUM GROUP submitted by JAMES RONALD SWEET in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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TO MY PARENTS

AND

MARCIA

ABSTRACT

The syntheses and reactions of compounds containing the rhenium group, $(\eta\text{-}C_5H_5)Re(CO)(NO)$- have been investigated. A series of stable, isolable complexes were prepared in which the metal center is bonded to a variety of organic molecules and functional groups. Structures and stereochemistry have been determined from infrared and NMR spectroscopy.

A number of nucleophiles attack the cation, $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$ (1) at the carbon of a carbonyl ligand. Reduction of 1 with a $NaBH_4$-THF-H_2O system afforded formyl, $(\eta\text{-}C_5H_5)Re(CO)(NO)(CHO)$ (2), hydroxymethyl $(\eta\text{-}C_5H_5)$-$Re(CO)(NO)CH_2OH$ (3), or methyl $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ (4) derivatives depending on the stoichiometry and reaction conditions. All possible reduction steps among 1, 2, 3 and 4 have been studied individually. Reduction of 1 with OH^- gave the hydroxycarbonyl, $(\eta\text{-}C_5H_5)Re(CO)(NO)(COOH)$ (6) which was decarbonylated to the hydride, $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5).

The chemistry of the hydride 5 is dominated by reactions which formally involve hydride (H^-) abstraction. The trityl cation Ph_3C^+ reacts with 5 in the presence of donor ligands L to give cations of the type $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$, L = CH_3CN, THF, Acetone. Reaction of 5 with Ph_3C^+ in CH_2Cl_2 resulted in formation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(3,4\text{-}\eta^2\text{-}C_6H_5\text{-}CPh_2H)]^+$ (13). The coordinated triphenylmethane of 13 is

displaced by PPh_3 to give $[(\eta\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]^+$, and deprotonated by Et_3N forming $(\eta\text{-}C_5H_5)Re(CO)(NO)$(*m*- and p-$C_6H_4\text{-}CPh_2H$). The hydride 5 will also react with tropylium cation, $C_7H_7^+$ to form $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+$ (18) which was deprotonated to $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22).

Dinuclear complexes $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)^+$ (19) and $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)^+$ (20) have been prepared and studied. Deprotonation of 20 afforded the dimer $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21), which exists in solution as a mixture of interconverting structures: bridged, nonbridged, and diastereomers due to chirality at each metal.

Cycloheptatrienyl, $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) and cyclopentadienyl, $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ (23) complexes have been prepared. Electrophilic attack on the cyclopolyenyl ring gave olefin complexes such as $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+$ 18 and $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_5H_6)]^+$ (27). The monohaptocyclopentadienyl compound 23 is fluxional and the pathway and stereochemistry of the metal migration were studied employing proton NMR spin saturation transfer experiments.

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LIST OF ABBREVIATIONS

Cp = η-cyclopentadienyl
Me = methyl
Bu = butyl
Ph = phenyl
THF = tetrahydrofuran
WGS = Water Gas Shift
δ = chemical shift in ppm's from tetramethylsilane
diphos = $Ph_2P-CH_2-CH_2-PPh_2$
dmpe = $Me_2P-CH_2-CH_2-PMe_2$

* * * * *

In addition, readers are reminded that according to I.U.P.A.C. nomenclature, the prefix η without superscript designates a structure in which all atoms of a ring or chain are bound to the central atom.

CHAPTER I

THE RHENIUM GROUP, $(\eta\text{-}C_5H_5)Re(CO)(NO)$-

This thesis describes the preparation and reactions of a series of organorhenium compounds, all of which contain $(\eta\text{-}C_5H_5)Re(CO)(NO)$-, referred to as "the rhenium group". A variety of functional groups and molecules will bond to this metal center to give stable isolable complexes. These compounds and their reactions demonstrate many of the processes central to modern organotransition metal chemistry. Investigation of the rhenium group has provided a comparison of a wide spectrum of compounds within the same metal system, an opportunity seldom encountered in this field. Before describing the chemistry of the rhenium group, a brief discussion of the development of organotransition metal chemistry will be presented.

SECTION I

ORGANOTRANSITION METAL CHEMISTRY

The student entering organotransition metal chemistry in the 1980's is confronted with a bewildering array of compounds and reactions. There is such a variety of metals, and an almost endless combination of ligands. At first sight, the structure and bonding modes found in many of these metal complexes appear to be contrary to the principles learned in other branches of chemistry. Surely a long time must have been required for the field to reach this advanced stage of development. This is true, as nearly 150 years have passed since the first reported organotransition metal complex. And yet, in this same area of study it is the rare compound whose existence spans a period of over 30 years. This paradox is one of the most important concepts todays' student need master to fully appreciate this challenging field.

The first preparation of organotransition metal complexes was reported by Zeise[1] in 1827. The compounds were ethylene complexes of platinum, $(C_2H_4)PtCl_2$, now known to be a chloro bridged dimer and $K[PtCl_3(C_2H_4)]$ commonly referred to as Zeise's salt. It was over 50 years before the next crucial discovery. In 1890, Mond[2] found that carbon monoxide would react with finely divided nickel to give a volatile liquid characterized as $Ni(CO)_4$, the first of the binary carbonyls.* The properties of this transition metal compound must have been very puzzling to nineteenth century chemists.

At the turn of the century the development of Grignard reagents provided an opportunity to prepare simple alkyl and aryl derivatives of the transition metals. It was found that transition metal halides did react with Grignard reagents but stable complexes could not be isolated. As similar reactions with main group metal halides had been successful, it was concluded that transition metal carbon bonds were inherently unstable. This misconception would persist for over 60 years and prove a major deterent to further studies.*

---

*The first transition metal carbonyl, $Pt(CO)_2Cl_2$ had actually been prepared 20 years earlier by Schutzenberger.[3]

In the first half of this century some development did occur in transition metal carbonyl chemistry. Many of the binary carbonyls were prepared but in general progress was slow. There is one very noteworthy exception to this statement; the work of W. Hieber.[6] Beginning in the 1930's, this German chemist performed experiments on metal carbonyls which were far ahead of their time. Hieber and co-workers were responsible for the preparation of many of the binary carbonyls, including $Re_2(CO)_{10}$,[7] the first carbonyl anions, and the first carbonyl hydrides. In the work of Hieber, one finds postulation of mechanisms, such as nucleophilic attack on coordinated carbon monoxide, which must have appeared very speculative at the time but today are widely accepted processes.

In 1951, the first reported preparation of biscyclopentadienyliron, $(\eta\text{-}C_5H_5)_2Fe$ appeared in the literature. This molecule prepared by Kealy and Pauson[8] is perhaps the single most important discovery in organotransition metal chemistry. Attempts to describe the structure of ferrocene in terms of the bonding theories developing at that time for olefin and carbonyl complexes led to the concept of the π-acid ligand. The realization that ligands such as carbon monoxide and π (now designated η) -cyclopentadienyl have both a sigma and pi contribution in their bonding to transition metals marks the beginning of modern organotransition metal chemistry.

---

*In hindsight, during this period evidence for stable transition metal carbon bonds already existed.[4,5]

The discovery of ferrocene was followed by the preparation of the first transition metal compounds containing both η-cyclopentadienyl and carbon monoxide groups. The use of a combination of these two ligands on the same metal, resulted in a virtual explosion in the number of reported organotransition metal complexes. In the period from the late 1950's to mid 1960's, many workers, but in particular the groups of G. Wilkinson and E. O. Fischer developed many of the basic synthetic methods so important to organotransition metal chemistry. The search for new and improved synthetic routes remains today a major theme for new research.

The next decade was a maturing period for organotransition metal chemistry. With a large number of compounds available for study, certain trends began to appear. To a degree it became possible to predict the properties of unknown compounds and design synthetic routes for their preparation. Structure and bonding theories rapidly developed during this period. The early empirical descriptions of bonding have been refined culminating in the molecular orbital calculations now available for many metal systems. The use of X-ray structural analysis has proven a valuable tool, particularly when correlated with spectroscopic methods. Infrared and NMR spectroscopy, first widely utilized in the 1950's, became indispensable for the characterization of new products. In the late 1960's and early 70's, many new ligands and functional groups were introduced. Basic starting materials, such as the binary carbonyls became commercially available, providing convenient entries to an otherwise somewhat inaccessible field.

It was during the early 1970's that the myth concerning the inherent instability of transition metal-carbon bonds was finally laid to rest.[5,9] With the widespread use of π acid ligands in the 1950's, several compounds, e.g., $(\eta\text{-}C_5H_5)Mo(CO)_3CH_3$, $CH_3Mn(CO)_5$ containing sigma M-C bonds had been prepared. It was assumed that the presence of π-acid ligands stabilized these complexes allowing formation of the otherwise unfavorable metal-alkyl bonds. As a number of other transition metal alkyls, some without π-acid ligands, appeared in the literature this argument no longer appeared valid. It became obvious that the lack of metal alkyl complexes was due, not to an inherent weakness of the M-C bond, but to the availability in many cases of low energy pathways to decomposition. Upon recognition of this property, it was possible to design new synthetic routes and ligands which would block these decomposition pathways. The result has been the isolation of a variety of transition metal alkyl and aryl complexes, some of which show excellent thermal stability.

Beginning in the mid-1970's, one can sense a change in the direction of organotransition metal chemistry. The interest in synthesis, structures, new types of complexes and the chemistry, per se remains of course very high. It seems however, that the emphasis today is placed on the utilization of new compounds and their relationship to other branches of science. Particularly important in this respect has been the use of metal complexes in organic syntheses and of organic reagents in organotransition metal chemistry. The combination of these two interrelated fields of study has been very beneficial to both disciplines and promises to remain so in the future.

A great influence in modern organotransition metal chemistry comes from the study of industrial catalytic processes. Isolated organotransition metal compounds can be used as models to provide information helpful in the development of metal catalysts for such essential industrial processes as hydroformylation; metathesis, isomerization and polymerization of olefins; hydrogenation of alkenes, alkynes, aromatics, nitrogen, carbon monoxide, and coal; as well as many others. The use of metal complexes themselves as homogeneous catalysts and catalytic precursors would be preferable in many ways to the present reliance on heterogeneous systems. Some of the compounds prepared in the previous decades are already in use commercially; others show promise.

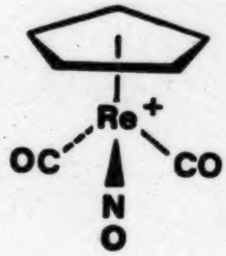
The study of organotransition metal compounds has come a long way since the early years of Zeise and Mond. This once obscure branch of transition metal chemistry has grown to become a distinct and highly developed field in its own right. No longer a little known study of misunderstood compounds, organotransition metal chemistry has come of age.

SECTION II

THE RHENIUM GROUP, $(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}$

This section discusses the brief history of the rhenium group. There is very little previously reported chemistry to be examined. Only two reactions of compounds containing the rhenium group were known; they are responsible for initiation of the present study. In addition, application of the 18-electron rule to $(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}$ compounds will be discussed.

The starting material for an investigation of the chemistry of the rhenium group is the cation, $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$:



This carbonyl cation, $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)][PF_6]$ was first reported in 1968 by E. O. Fischer and H. Strametz.[10] The compound was obtained in 64% yield by reaction of $(\eta\text{-}C_5H_5)Re(CO)_3$ with $NOHSO_4$, followed by exchange of the HSO_4^- counter ion for PF_6^- [Eq (1)]. Characterization

$$(\eta\text{-}C_5H_5)Re(CO)_3 + NOHSO_4 + NH_4PF_6 \longrightarrow [(\eta\text{-}C_5H_5)Re(CO)_2(NO)][PF_6] + CO + NH_4HSO_4 \quad (1)$$

included infrared and ^{1}H NMR spectroscopy and elemental analysis. This reaction [Eq (1)] occurs with electrophilic substitution of one of the carbonyl ligands of $(\eta\text{-}C_5H_5)$-$Re(CO)_3$ by NO^+. The process may proceed by direct attack of NO^+ at rhenium or by prior dissociation of carbon monoxide to give coordinately unsaturated $(\eta\text{-}C_5H_5)Re(CO)_2$. Fischer and Strametz noted the thermal and oxidative stability of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ but reported no reactions of the compound.

In 1971, N. Okamoto[11] developed an improved preparation of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)][PF_6]$. During an exploration of new synthetic routes to transition metal nitrosyls, Okamoto discovered the rhenium cation was conveniently obtained from reaction of $(\eta\text{-}C_5H_5)Re(CO)_3$ with $NOPF_6$ in acetonitrile. A variation of this reaction was used in the present study to prepare $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$. It was found that the yield and quality of the product could be increased by the use of $NOBF_4$ with nitromethane as a solvent. The methods used to prepare and purify $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)][BF_4]$ are described in the experimental section of Chapter II.

The first and at the beginning of this study, the only reactions of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ were reported in 1972 by Stewart, Okamoto and Graham.[12] These workers prepared the corresponding hydride $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ and methyl $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ compounds. The hydride was obtained by reaction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)][PF_6]$ with Et_3N/H_2O followed by heating [Eq (2)]. The methyl

$$[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+ \begin{cases} \xrightarrow[\text{acetone},\Delta]{Et_3N/H_2O} (\eta\text{-}C_5H_5)Re(CO)(NO)H & (2) \\ \xrightarrow[\text{THF}]{NaBH_4} (\eta\text{-}C_5H_5)Re(CO)(NO)CH_3 & (3) \end{cases}$$

compound was prepared by reduction of the carbonyl cation with $NaBH_4$ in *anhydrous* THF [Eq (3)]. Both of these neutral products showed very high thermal and oxidative stability, a property now known to be characteristic of compounds containing the rhenium group.

The results of this study were a great surprise to Graham and co-workers. The products of these reactions contrast sharply with those which had previously been reported for the analogous manganese cation, $[(\eta\text{-}C_5H_5)Mn(CO)_2(NO)]^+$. Under conditions similar to those of Eq (2)[13] or (3)[14] the Mn compound had been shown to give the dimer $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ presumably by way of unstable mononuclear species. It was also known[13] that the carbonyls of $[(\eta\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ were readily displaced thermally by other two electron ligands. No such reaction has ever been reported for $[(\eta\text{-}C_5H_5)Re(CO)_2\text{-}(NO)]^+$. These results indicate the third row metal, Re greatly enhances thermal stability and bond strengths in the $(\eta\text{-}C_5H_5)M(CO)(NO)$-system.

A reinvestigation of the reactions shown in Eqs (2) and (3) was the original aim of the present study. The nature of the products formed in these reactions suggested that intermediate complexes had been formed. This is particularly true for the $NaBH_4$ reaction where a coordinated CO ligand has been reduced to a methyl group. After completion of this initial goal (Chapter II) it became obvious that a great deal more chemistry of the rhenium group remained to be explored. The results of these further studies are described in Chapters III and V.

* * * * *

The rhenium group forms cations of the type $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$, where L is a two electron donor ligand or neutral species, $(\eta\text{-}C_5H_5)Re(CO)(NO)R$ where R is a one electron ligand. The carbonyl cation is an example of the first group, L = CO; the neutral hydride and methyl, R = H, CH_3 demonstrate the second. Both these formulations conform to the 18-electron rule, one of the fundamental tenets of organotransition metal chemistry.

It has long been noted that the vast majority of stable transition metal compounds containing π-acid ligands have eighteen bonding electrons about the metal. This observation is sufficiently general that it has often been used as a guideline to postulate the number of ligands a transition metal will coordinate and the type of bonding the ligands will employ. It is unfortunate that the 18-electron rule, also called the Inert Gas or Effective Atomic Number Rule is even today often presented as an empirical statement without a theoretical explanation. This practice may give the reader the impression that, compared to the other elements there is something unusual about transition metals. In reality the 18-electron rule is analogous to the octet rule of main group chemistry.

From a molecular orbital view, stable compounds are those in which the bonding M.O.'s are occupied. If an element makes use of all its valence orbitals when forming a compound, the number of electrons required to fill the bonding M.O.'s will be equal to the number of electrons in the outer shell of the next higher noble gas. Carbon, for example, forms stable compounds of the type CR_4, where each R group can be considered a one electron donor. The four bonding orbitals of the carbon atom can be combined with four orbitals provided by the

R groups to give a total of eight molecular orbitals. The four bonding M.O.'s will be occupied by the four valence electrons of carbon plus the four electrons provided by the R groups to give an eight electron complex. The number of electrons available to carbon is the same as that of the noble gas neon.

The situation is similar for a transition metal but a greater number of orbitals are available for bonding. Rhenium is a third row transition metal in Group VIIa. The number of valence shell orbitals on rhenium is nine; one 6s, three 6p and five 5d. If rhenium uses all nine orbitals, they will be combined with nine suitable ligand orbitals to form eighteen molecular orbitals, nine bonding and nine antibonding. To fill the bonding molecular orbitals rhenium would form complexes in which there are eighteen valence electrons. The rhenium atom itself has seven outer shell electrons, the other eleven electrons must be provided by the ligands to which the metal is coordinated.

The rhenium group $(\eta\text{-}C_5H_5)Re(CO)(NO)$- contains an η-cyclopentadienyl group, one carbonyl and one nitrosyl ligand. When pi bonded to a transition metal the cyclopentadienyl group donates five electrons. Carbon monoxide with a lone pair on carbon, donates two electrons to the metal. The nitrosyl group, in compounds of this type,[15] is considered a three-electron donor. The rhenium group $(\eta\text{-}C_5H_5)Re(CO)(NO)$- thus has 7 + 5 + 2 + 3 = 17 valence electrons. Stable compounds are formed, that is all bonding orbitals are filled, when this fragment coordinates a single one-electron ligand to give neutral $(\eta\text{-}C_5H_5)Re(CO)(NO)R$ species or one two-electron ligand to give *cations* $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$. The electron count in each of these formulations is demonstrated below for $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ and $[(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$.

$[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$

Re = $7e^-$
$\eta\text{-}C_5H_5$ = $5e^-$
2 x CO = $4e^-$
NO = $3e^-$

$19e^- - 1e^- = 18e^-$

$(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$

Re = $7e^-$
$\eta\text{-}C_5H_5$ = $5e^-$
CO = $2e^-$
NO = $3e^-$
CH_3 = $1e^-$

Total = $18e^-$

The 18-electron rule was initially formulated by Sidgwick[16] in 1934, after a study of the binary carbonyls. Few exceptions are known among compounds containing π-acid ligands. In complexes which have only sigma donor ligands, stable complexes with fewer than eighteen electrons are often formed due to incomplete use of the metals' valence shell orbitals. A discussion of this aspect of the 18-electron rule and its relationship to metal catalysis has been published by Tolman.[17] For a discussion from the molecular orbital viewpoint the reader is referred to a 1969 paper by Mitchell and Parish.[18]

"Electron bookkeeping" can be an invaluable aid when formulating structures for newly prepared compounds. Among the complexes of the rhenium group there are no known exceptions to the 18-electron rule. This is not to suggest that species with fewer than 18 electrons could not be formed. Many reactions of the rhenium group appear to occur *via* intermediates which would have 16 electrons. Such intermediates are expected to be high-energy forms with limited lifetimes under ordinary conditions.

SECTION III

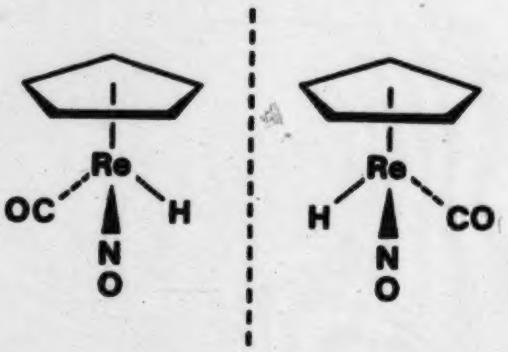
OPTICAL ISOMERS OF COMPOUNDS CONTAINING THE RHENIUM GROUP.

The study of optical activity in transition metal chemistry began with the resolution of an optically active, octahedral complex, $[Co(en)_2(NH_3)Cl]^{++}$ (en = ethylenediamine) by Werner[19] in 1911. Recognition of this property has proven a valuable aid in stereochemical studies of Werner-type metal complexes.[20] Optical activity in organotransition metal compounds is a much more recent and less developed subject.

It was perhaps first pointed out by Hieber[21] in 1963 that an organometallic compound with four different ligands arranged in a tetrahedral geometry would be nonsuperimposable on its mirror image. The resolution of such optical isomers arising from chirality at the metal center was first accomplished in 1969.[22] The compound described in this report, $[(\eta\text{-}C_5H_5)Mn(CO)(NO)(PPh_3)]BF_4$ has a pseudo-tetrahedral structure and thus exists as a pair of enantiomers. From the time of this initial discovery a number of papers have appeared documenting this type of isomerism with a variety of metal complexes. Today, chirality at the metal center is recognized as a useful probe for mechanistic studies in organotransition metal chemistry. For a summary of the historical development and recent advances in this area the reader is referred to a comprehensive 1980 review article by Brunner.[22]

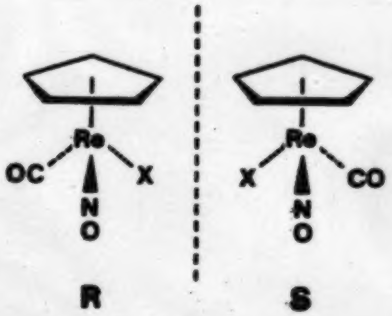
(1) Optical Isomers in Mononuclear Compounds of the Rhenium Group. The compounds prepared in this study all contain the rhenium group, $(\eta\text{-}C_5H_5)Re(CO)(NO)$-. On coordination of a fourth different ligand to the rhenium group a chiral center is generated at the metal. Compounds of this type, CpRe(CO)(NO)X, are expected to have a pseudo-tetrahedral geometry and are thus non-superimposable on their mirror images.

A compound such as $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ has two possible configurations as shown below. These molecules are enantiomers, they differ only in the arrangement of the ligands about the metal center. The enantiomers of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ should have identical physical properties including their infrared and NMR spectra. They



would be expected to rotate plane polarized light equally in opposite directions.

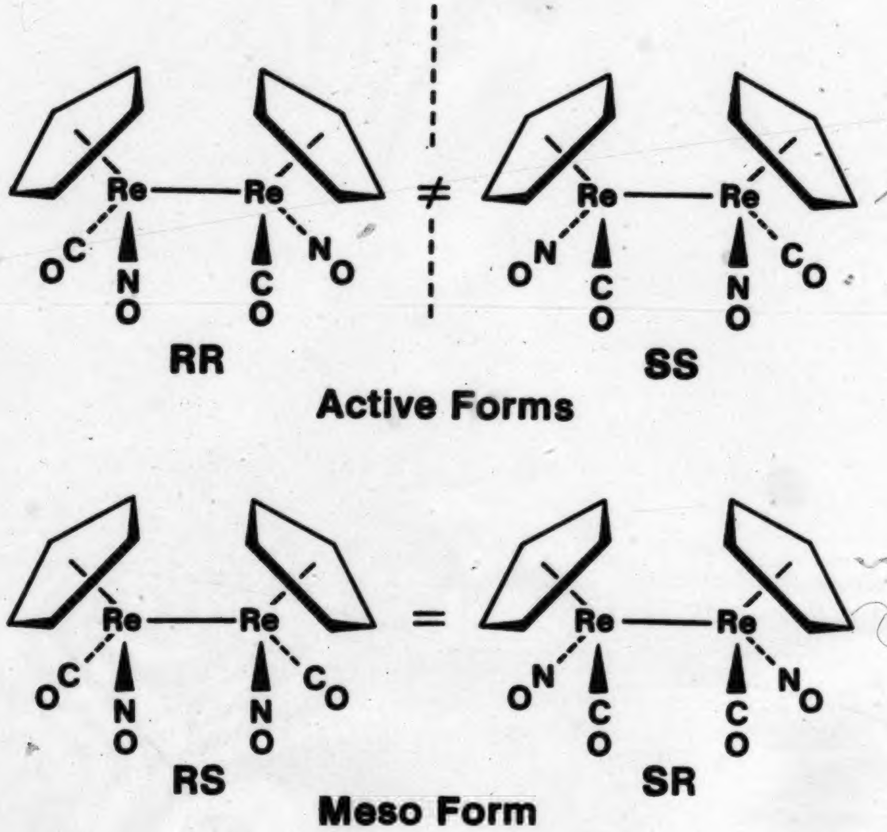
It is convenient to have a notation describing the configuration at the metal center. In this thesis a variation of the R/S nomenclature[23] of organic chemistry will be used. The priority of the ligands in a compound of the type CpRe(CO)(NO)X, will be defined as Cp>NO>CO>X, regardless of the nature of the group X. Positioning a structure with the ligand X away from the viewer, the configuration is R if the direction on moving from higher to lower priority among the other groups is *clockwise* and S if the direction is *counterclockwise*. Use of the R/S nomenclature in this modified manner avoids confusion when relating the configurations of different compounds. All compounds of the rhenium group with the same label have the same absolute configuration.



No attempt has been made to resolve enantiomers of compounds containing the rhenium group. However, the existence of an asymmetric center can be detected in certain of the mononuclear complexes. On coordination of a ligand of the type $-CR_2X$ to $(\eta-C_5H_5)Re(CO)(NO)-$, the two R groups will be rendered nonequivalent and are said to be diastereotopic. Regardless of the rotamer in which the molecule resides or the speed of rotation about the Re-CR_2X bond the R groups remain nonequivalent. Diastereotopic R groups can in some cases be detected by NMR, confirming the presence of the asymmetric metal center. Examples of CpRe(CO)(NO)X compounds containing diastereotopic groups on the ligand X can be found in Chapters II and V.

(2) Optical Isomers in Dinuclear Compounds of the Rhenium Group. A number of complexes have been prepared in this study which contain two units of the rhenium group. The presence of two asymmetric metal centers gives rise to a maximum of four isomers. These isomers correspond to permutations of the two possible configurations for each rhenium center in such a dinuclear complex.

An example of this type of isomerization is provided by the dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. This compound contains two units of the rhenium group, held together by a metal-metal bond. Optical isomers for the cis structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ in which the CO and NO ligands are terminally bonded are shown in Scheme 1. In each of the top structures of Scheme 1, the two metal centers have the same configuration. There are two such isomers, RR and SS which are nonsuperimposable mirror images and thus *enantiomers*. These isomers, referred to as the active forms, would have the same infrared and NMR spectra.

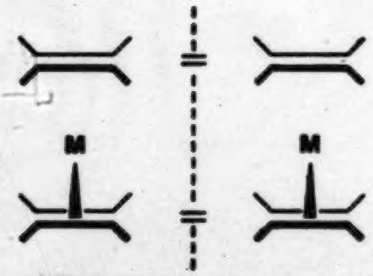

Re
Re
OC
NO
CO
NO
≠
Re
Re
ON
CO
NO
CO
RR
SS
Active Forms
Re
Re
OC
NO
NO
CO
=
Re
Re
ON
CO
CO
NO
RS
SR
Meso Form

Scheme 1

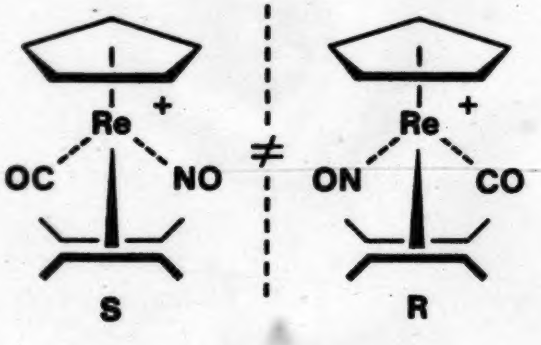
The RS and SR structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ each contain metal centers with the opposite configurations. In this case the mirror images are superimposable, and thus only one isomer is formed. This isomer, referred to as the Meso form, contains a plane of symmetry and is optically inactive. The meso and active forms are *diastereomers*. They are physically and chemically distinct and would have different spectroscopic properties.

The lack of optical activity in the Meso form of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$, is due to a plane of symmetry which bisects the Re-Re bond and reflects the two ends of the molecule. If the Meso form were drawn with a trans structure, the compound would have a center of symmetry and again be optically inactive. The presence of these symmetry elements reduces to three the number of optical isomers for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. A derivative of the rhenium dimer in which these symmetry elements are absent, for example trans-$[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)^+$ would have four optical isomers. Such a compound would exist as two diastereomers each composed of an enantiomeric pair. The dinuclear derivatives of the rhenium group are discussed in Chapter III.

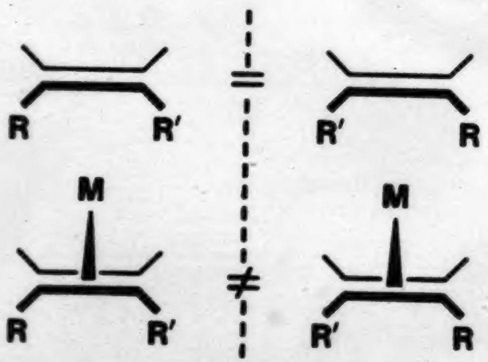
(3) Optical Isomers with Olefin Complexes. A symmetrically substituted olefin, for example ethylene has D_{2h} symmetry. Such a compound has three mirror planes and a center of symmetry and is identical to its mirror image. If a transition metal (M) is coordinated to one face of such an olefin, the symmetry of the resulting adduct is C_{2v}. The metal complex has two planes of symmetry and is also superimposable on its mirror image.



If the rhenium group were coordinated to a D_{2h} olefin the resulting complex would have one center of asymmetry (Re) and exist as two enantiomers.

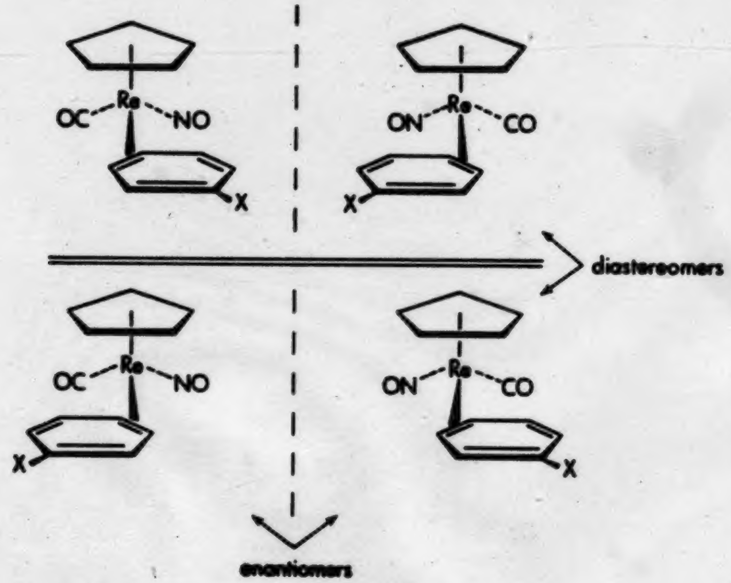


A different situation exists with an olefin containing two different groups in a cis configuration and C_s symmetry. Olefins of this type have a plane of symmetry and are identical to their mirror images. On coordination of a metal to one face of such an olefin the mirror plane is removed and the symmetry reduced to C_1. The metal-olefin complex would have an asymmetric structure and form as a pair of enantiomers.



Coordination of the rhenium group to a double bond with this type of substitution creates a further center of asymmetry.* There are two possible diastereomers, each composed of an enantiomeric pair (Scheme 2). The diastereomers would be chemically and physically distinct compounds with different infrared and NMR spectra. This type of isomerism is encountered with the compounds discussed in Chapters III and V.

Scheme 2:


OC
Re
NO
X
ON
Re
CO
X
diastereomers
OC
Re
NO
X
ON
Re
CO
X
enantiomers

---

[*] A similar result has been obtained with a metal group containing a chiral ligand.[24]

CHAPTER II

THE REDUCTION OF COORDINATED CARBON MONOXIDE

SECTION I

INTRODUCTION

A. The Fischer-Tropsch Process

The study of models for catalytic reaction intermediates has often stimulated the development of new areas of organotransition metal chemistry. From the late 1970's, one of the most active fields of research has involved reactions in which coordinated carbon monoxide is reduced. The present chapter discusses the reactions of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ and their relationship to the catalytic conversion of carbon monoxide and hydrogen to hydrocarbons.

As a result of the steady increase in the price of crude oil since 1973, and a recognition that petroleum reserves are finite; more attention has focused on coal as an energy source and a feedstock for chemical industry. Although coal is plentiful and as yet relatively inexpensive, its use in the modern world presents some difficult problems. The burning of coal, as practiced in the last century, would cause serious environmental damage. There are a number of economic barriers, including the cost of transporting this relatively low efficiency fuel, and the modification of presently oil based systems to the use of coal. A much more attractive approach[25] would be the conversion of coal into liquid products and gas. Fortunately, the principles of this technology already exist.

As long ago as 1869, Berthelot[26] performed the first experiments on the direct hydrogenation of coal. On an industrial scale a more feasible approach is the conversion of coal in the presence of water to a mixture of CO and H_2, called synthesis gas. With the aid of certain transition metal catalysts, synthesis gas can be converted to a liquid product containing alkanes, alkenes, alcohols, aldehydes, ketones, and acids.

The development of the present process can be traced to the pioneering studies of Fischer and Tropsch who, in 1925 reported[27] the first catalyst, an iron/zinc oxide system capable of producing predominantly higher hydrocarbons at atmospheric pressure. Today the conversion of synthesis gas to hydrocarbons is often referred to as the Fischer-Tropsch synthesis. Utilization* of the Fischer-Tropsch process reached a peak in wartime Germany and virtually disappeared in the 1950's with the advent of cheap oil, coupled with rising coal costs.

The present world energy crisis has brought renewed interest in the production of liquid fuel from coal.

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*The development of industrial Fischer-Tropsch catalysts has been extensively reviewed elsewhere.[28]

In recent years, research has focused on the development of homogeneous Fischer-Tropsch catalysts.* A homogeneous process should give greater product selectivity and milder reaction conditions; key economic considerations. The search for such homogeneous catalysts and model compounds for mechanistic study, forms an important part of metal carbonyl chemistry today.

B. Mechanisms of the Fischer-Tropsch Process

The first step in the Fischer-Tropsch synthesis requires combustion of a coal-water slurry to generate a carbon monoxide-hydrogen mixture, typically ca. 1:1. For the production of hydrocarbons and alcohols, a higher H_2:CO ratio is desirable as can be seen from Eq (4) and (5).

$$n\,CO + 2nH_2 \longrightarrow (CH_2)_n + nH_2O \qquad (4)$$

$$n\,CO + (n+1)H_2 \longrightarrow H(CHOH)_nH \qquad (5)$$

One method of hydrogen enrichment of synthesis gas is the water gas shift (WGS) reaction [Eq (6)]

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (6)$$

To proceed at a reasonable rate, the WGS reaction requires a transition metal catalyst. Following removal of CO_2 and other impurities the hydrogen-rich synthesis gas is heated under pressure with transition metal catalysts to give a range of organic products depending on the exact conditions.[30]

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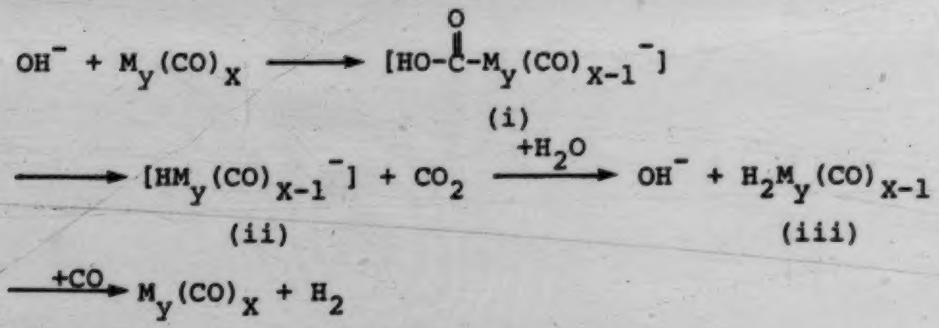
*For a recent discussion of the search for homogeneous Fischer-Tropsch catalyst see reference 29.

Mechanisms have recently been suggested for both the Fischer-Tropsch and WGS reactions, based on all the available data. These reaction schemes include as far as possible intermediates and reactions known in the solution chemistry of discrete transition metal complexes. This conforms to the view, first suggested by Nyholm,[31] of considering heterogeneous catalysts as comprising individual active sites and their coordination chemistry, rather than the classical "active surfaces".

The WGS reaction is catalytic in the presence of basic aqueous alcoholic solutions of certain transition metal carbonyls. The sequence shown in Scheme 3 has been proposed by R. M. Laine[32] to account for the catalytic conversion of H_2O and CO to H_2 and CO_2.

Scheme 3:



$$OH^- + M_y(CO)_X \longrightarrow [HO-\overset{O}{\overset{\|}{C}}-M_y(CO)_{X-1}^-] \quad \text{(i)}$$

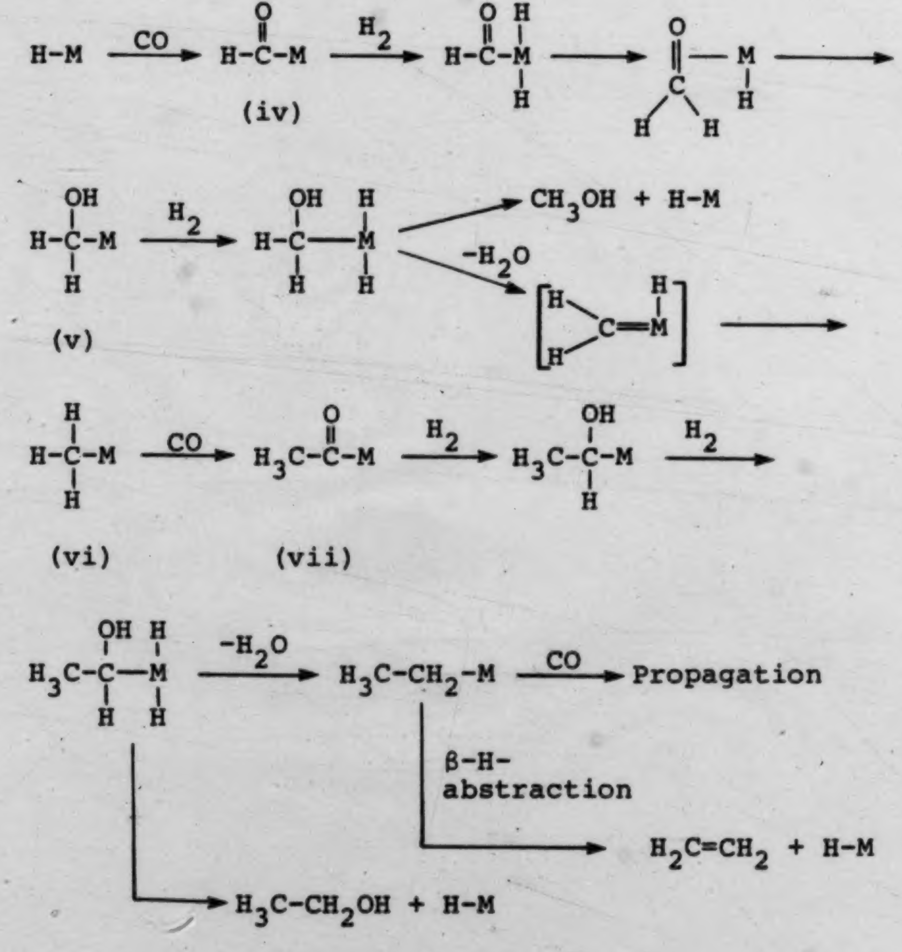
$$\longrightarrow [HM_y(CO)_{X-1}^-] + CO_2 \xrightarrow{+H_2O} OH^- + H_2M_y(CO)_{X-1} \quad \text{(ii)} \quad \text{(iii)}$$

$$\xrightarrow{+CO} M_y(CO)_X + H_2$$

The initial step involves nucleophilic attack by hydroxide ion (basic solution) on coordinated carbon monoxide to give an hydroxycarbonyl complex (i). The metallocarboxylic acid (i) decarboxylates, releasing CO_2 and forming an anionic metal hydride (ii). The metal hydride (ii) is protonated by another water molecule giving a dihydride complex (iii) which would be expected to eliminate hydrogen readily, forming a coordinately unsaturated species "$(M_y(CO)_{X-1})$". Attack by CO on the $M_y(CO)_{X-1}$ complex regenerates the catalyst precursor to complete the cycle. In basic media one might expect the hydroxycarbonyl complex to exist as the carboxylate anion, or perhaps as $[\mathrm{O{-}\overset{O}{\overset{\|}{C}}{-}M_y(H)(CO)_{X-1}}]^-$. As discussed in Section III-B there is some question as to the mechanism by which metallocarboxylic acids decarboxylate. In the present work stable examples of some of the species suggested in this mechanism have been prepared and their properties discussed.

During the past 50 years a number of mechanisms have been proposed for the Fischer-Tropsch synthesis depending on the catalyst used and the products obtained. More recently attempts have been made to suggest a unified reaction mechanism. An oft quoted scheme reported in 1976 by Henrici-Olivé and Olivé[30] is of particular significance to the present work. After a thorough study of reaction conditions, catalysts, and product distributions, the mechanism shown in Scheme 4 was proposed. The authors have accounted for all primary products formed in Fischer-Tropsch syntheses using wherever possible reactions and intermediates known from organotransition metal chemistry.

Scheme 4:


H-M
CO
H-C-M
(iv)
H2
H-C-M
(v)
CH3OH + H-M
-H2O
C=M
(vi)
H3C-C-M
(vii)
H3C-CH2-M
Propagation
β-H-abstraction
H2C=CH2 + H-M
H3C-CH2OH + H-M

Key intermediates in this scheme contain coordinated formyl (iv), hydroxymethyl (v), methyl (vi) and acyl (vii) ligands. Model compounds for all these intermediates have been isolated in the present study. The reactions and properties of these complexes in relation to previous studies will now be discussed.

Section II

THE REDUCTION OF COORDINATED CARBON MONOXIDE TO FORMYL, HYDROXYMETHYL AND METHYL LIGANDS

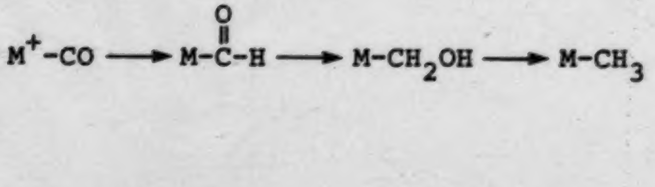
A. Introduction

The stoichiometric reduction of a coordinated carbonyl to methyl was first demonstrated in 1967 by Treichel and Shubkin.[33] These authors found that treatment of $[(\eta\text{-}C_5H_5)M(PPh_3)(CO)_3{}^+]$, where M = Mo or W, with sodium borohydride in anhydrous tetrahydrofuran, gave $(\eta\text{-}C_5H_5)\text{-}M(PPh_3)(CO)_2CH_3$ [Eq (7)]. The relatively high yields

$$[(\eta\text{-}C_5H_5)M(PPh_3)(CO)_3]^+ \xrightarrow{NaBH_4} (\eta\text{-}C_5H_5)M(PPh_3)(CO)_2CH_3 \qquad (7)$$

M = Mo, W.

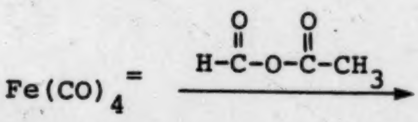
(69% for W and 27% for Mo) suggested the methyl ligand arose from reduction of a carbonyl group. In 1972, Graham and co-workers[12] reported a similar reaction with $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ to give the neutral methyl derivative again in high yield (50%). It was postulated that these reactions occurred with the intermediacy of formyl and hydroxymethyl complexes [Eq (8)] although no such



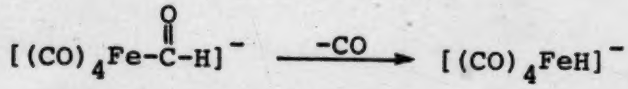
$$M^+\text{-}CO \longrightarrow M\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \longrightarrow M\text{-}CH_2OH \longrightarrow M\text{-}CH_3 \qquad (8)$$

species were isolated. It is noteworthy that the above preparation called for the use of excess $NaBH_4$ (greater than three moles); however, no attempts were made to determine the true stoichiometry.

These reactions remained anomalies in the literature, attracting little attention, until the late 1970's. At this time the search for stable, isolable intermediates in the reduction of coordinated carbon monoxide began in earnest. The first formyl complex had actually been reported in 1973 by Collman and Winter.[34] Treatment of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$, with acetic formic anhydride, [Eq (9)], cleanly afforded the anionic



$$Fe(CO)_4^{=} \xrightarrow{H-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3} [(CO)_4Fe-\overset{O}{\overset{\|}{C}}-H]^- \qquad (9)$$



$$[(CO)_4Fe-\overset{O}{\overset{\|}{C}}-H]^- \xrightarrow{-CO} [(CO)_4FeH]^- \qquad (10)$$

formyl $[(CO)_4FeCHO]^-$. Although stable in the solid state, the formyl complex decarbonylated in THF solution, [Eq (10)], to give the hydride, $[(CO)_4FeH]^-$, ($t_{1/2}$ (25°C) $\geq$ 12 days (THF)). In 1976, Collins and Roper[35] reported the first neutral formyl, $Os(CHO)Cl(CO)_2(PPh_3)_2$, obtained from hydrolysis of the corresponding thioformyl. The osmium complex also rapidly decomposed in solution to give the hydride. These reports established the existence of formyl complexes, and suggested their lack of stability was due to a low energy pathway to decomposition (i.e., decarbonylation).*

The preparation of formyls by direct reduction of coordinated carbon monoxide was first reported in 1976 by Casey and Neuman.[37] These authors described a straightforward route to a wide range of anionic formyls *via* the reaction of metal carbonyls with trialkoxyborohydrides [Eq (11)]. There followed a series of papers

$$[HB(OR)_3]^- + L_xM(CO) \longrightarrow B(OR)_3 + [L_xM(CHO)]^- \qquad (11)$$

L = PPh_3, $P(OPh)_3$, CO; R = CH_3, $CH(CH_3)_2$; M = Fe, Cr, W.

by various workers[38] which established the above as a general reaction of transition metal carbonyls.

The vast majority of these anionic formyl complexes rapidly decompose below room temperature, and must be characterized spectroscopically in the presence of boron byproducts. Thus, it was not feasible to explore their role in carbon monoxide reduction.

---

*It had long been known that certain transition metal hydrides could be prepared by hydridic reduction of the corresponding carbonyl cations, (e.g., $[(\eta\text{-}C_5H_5)Fe(CO)_3]^+ + NaBH_4 \rightarrow (\eta\text{-}C_5H_5)Fe(CO)_2H$.[36] At the time (1961) the possibility of a formyl intermediate in reactions of this sort had evidently not been considered. In retrospect, such a reaction may well involve initial formation of a formyl complex, followed by decarbonylation.

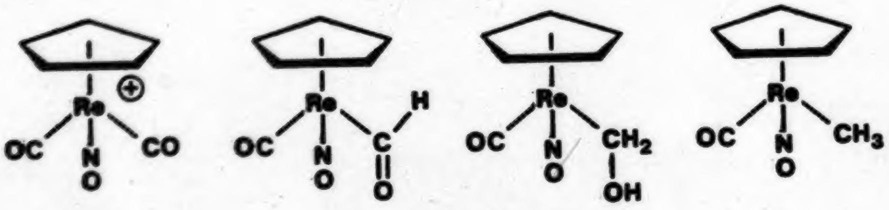
Hydroxymethyl complexes have proven even more elusive than formyls. Indeed until the present study, some workers[39] expressed serious doubts about the existence of such a complex in the stepwise reduction of carbon monoxide. Two substituted hydroxymethyl complexes have been reported, $(\eta\text{-}C_5H_5)(OC)_2FeC(CF_3)_2OH$,[40] and the very unstable $(OC)_5MnCH(C_6H_5)OH$,[41] which has been suggested as a reaction intermediate. In 1970, the preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ was claimed by Nesmeyanov[42] from the reaction of 1.3 moles of $NaBH_4$ with one mole of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ in benzene/H_2O. Identification was made by infrared spectroscopy, and elemental analysis. Attempts to reproduce this work in the present study[43] and in other laboratories[39,44] have been unsuccessful. It now appears that the original report was in error.

The present study was undertaken to reinvestigate the reactions of $NaBH_4$ with $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (**1**) and to show the existence or nonexistence of any formyl **2** or hydroxymethyl **3** intermediates (Scheme 5).

B. Reactions of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$ with Sodium Borohydride - Preparation of Formyl, Hydroxymethyl and Methyl Complexes

The reaction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (**1**) with *one mole* of sodium borohydride in the *presence of water* led

Scheme 5:



1 2 3 4

to the isolation of a neutral formyl complex $(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$ (2) in 62% yield. The formyl compound is an orange, air stable, microcrystalline solid of rather low thermal stability. In the solid state 2 is stable to ca. -10°C; in dilute solutions a slow decarbonylation occurs to give $(\eta\text{-}C_5H_5)Re(CO)(NO)H$, among other products.*

The identity of 2 was established by infrared and proton NMR spectroscopy. The medium intensity ν(CHO) stretch occurs at 1635 cm^{-1} (hexane), similar to that found in transition metal acyl derivatives. The proton NMR (methylcyclohexane-d_{14}) showed a characteristic low field signal at 16.2 ppm for the formyl hydrogen. The thermal instability of the formyl complex prohibited use of mass spectroscopy and elemental analysis.

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*The decomposition products of 2 are discussed in Section II-E.

Reaction of cation **1** with *two moles* of sodium borohydride in the *presence of water* gave the first authentic transition metal hydroxymethyl complex, $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ (**3**) in 70% yield. The hydroxymethyl compound **3** forms as orange, air stable, crystals which unlike the formyl complex **2** show excellent thermal stability (MP 95-96°C, sealed capillary under N_2).

The infrared and mass spectra of **3** (see Experimental, Section II) are totally consistent with its formulation as the hydroxymethyl compound. A satisfactory elemental analysis was also obtained. The proton NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ (**3**) is shown in Figure 1 . The presence of an asymmetric metal center renders the methylene protons nonequivalent. Thus, the proton NMR was definitive, showing a sharp singlet (5 H) at 5.88 ppm $(\eta\text{-}C_5H_5)$ and an ABX pattern for the CH_2OH group ($\delta(H_A)$ 5.14, $\delta(H_B)$ 5.55, $\delta(H_X)$ 3.94 ppm; $^3J_{AX}$ 6.1, $^3J_{BX}$ 5.5, $^2J_{AB}$ 9.3 Hz).

The reaction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (**1**) with *one mole* of sodium borohydride under *anhydrous conditions* gave the previously reported[12] methyl complex $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ (**4**) in 88% yield. The methyl

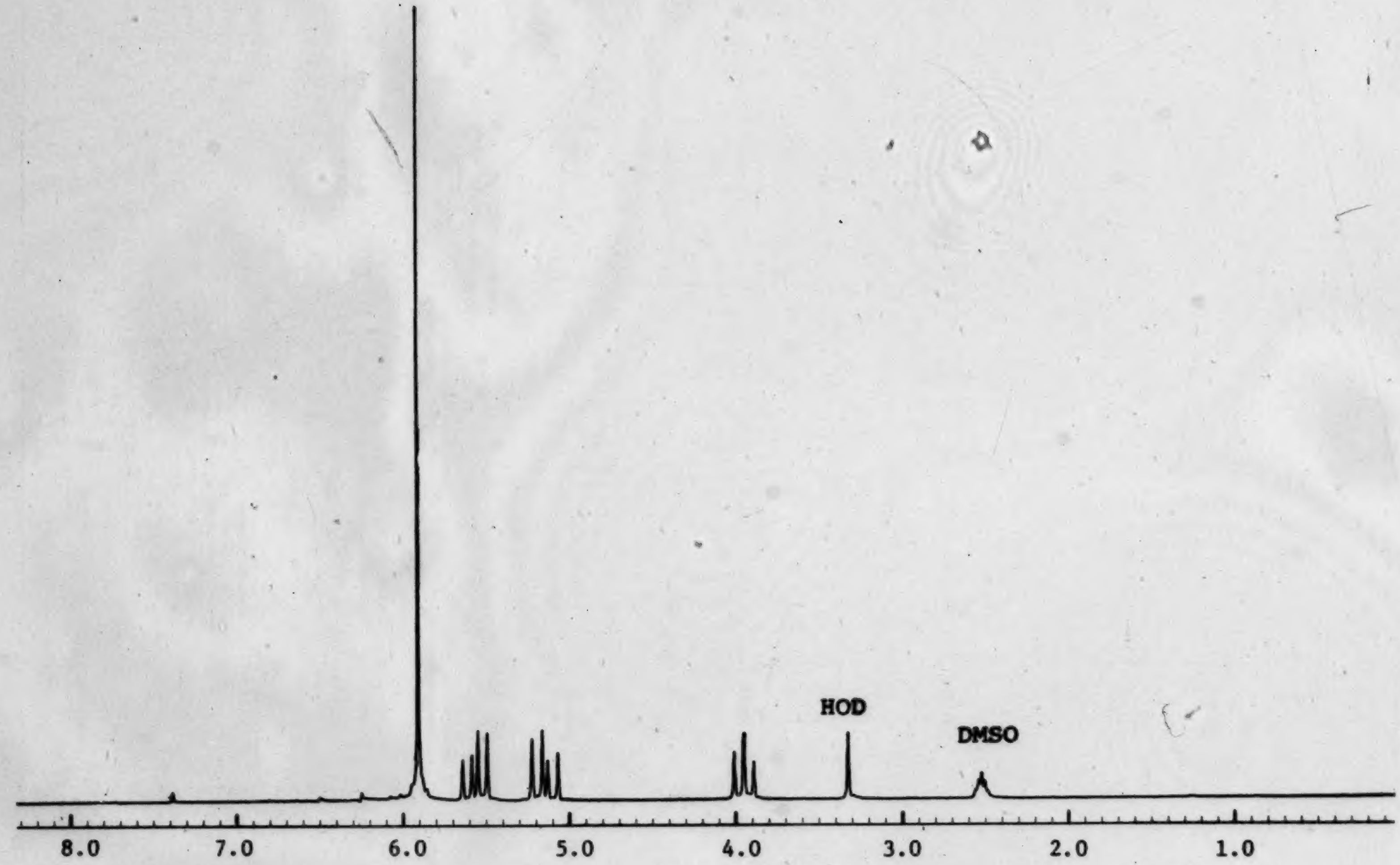
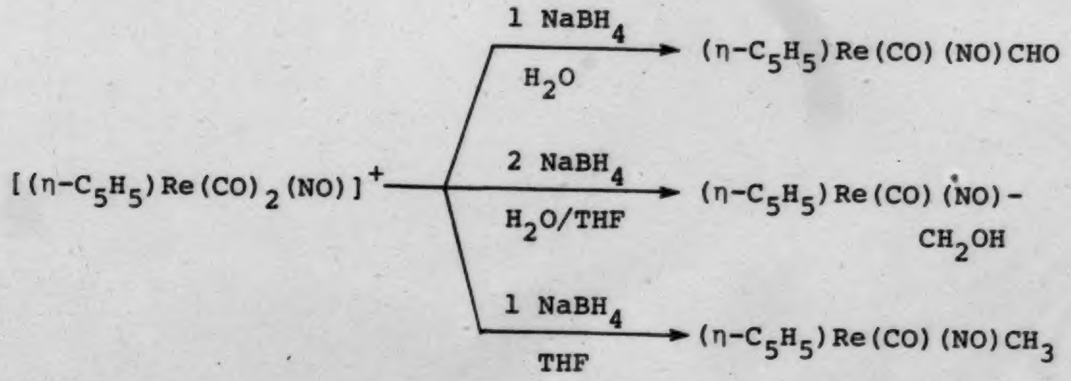


FIGURE I. ^1H NMR of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$, 100 MHz, DMSO-$d_6$.

compound formed as red crystals exhibiting good air and thermal stability, MP 75-76°C. The identity of 4 was established by comparison of its infrared, proton NMR and mass spectra to literature values.

The original Stewart, Okamato and Graham[12] preparation of 4 involved the use of a large (~10 fold) excess of $NaBH_4$. These conditions result in some product decomposition and left the stoichiometry of the reaction in doubt. It has now been established that only *one mole* of $NaBH_4$ is required for complete reduction of the cationic carbonyl 1 to the methyl 4. Use of the proper quantity of borohydride also gives a much higher yield of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ (88% *versus* 50%). The reactions of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (1) are summarized in Scheme 6.

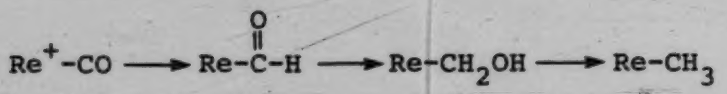
Scheme 6:



$[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$
1 $NaBH_4$
H_2O
$(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$
2 $NaBH_4$
H_2O/THF
$(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}CH_2OH$
1 $NaBH_4$
THF
$(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$

C. The Stepwise Reduction of Coordinated Carbon Monoxide

The preparations discussed in Section II-B demonstrate all the compounds one would expect to obtain from the hydridic reduction of a coordinated carbon monoxide [Eq (12)]. This is the first instance in which models



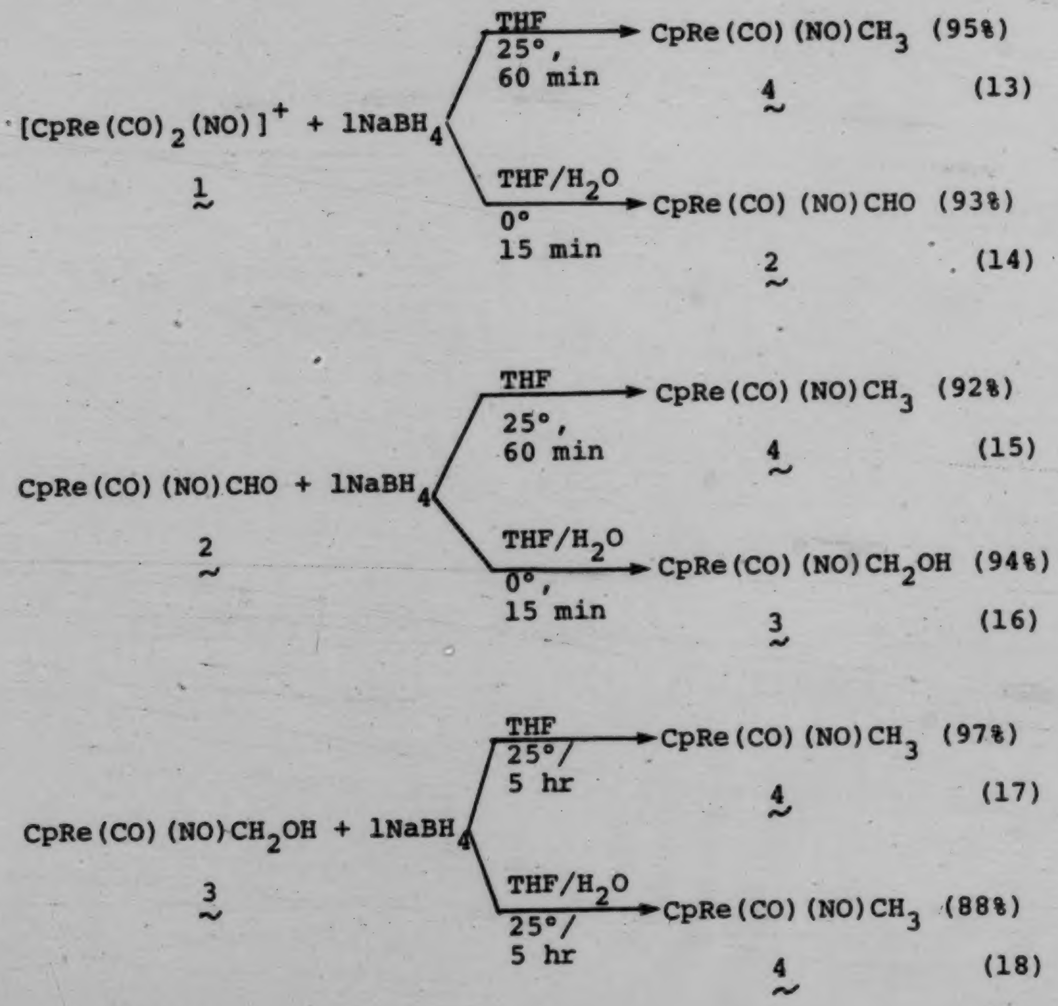
$$Re^{+}\text{-}CO \longrightarrow Re\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \longrightarrow Re\text{-}CH_2OH \longrightarrow Re\text{-}CH_3 \qquad (12)$$

for all presumed Fischer-Tropsch stages[30,45] have been isolated. In an attempt to better understand the mechanisms of these reactions and the various modes of reaction exhibited by $NaBH_4$, all the possible reduction steps among compounds **1**, **2**, **3** and **4** have been studied individually. If the exact stoichiometry of each reduction were to be established, product losses had to be minimized. Such losses would occur due to product instability and preparative workup. For this reason the reduction products were monitored by proton NMR, and yields obtained by integration *versus* an internal standard as outlined in the Experimental. Reactions and yields are summarized in Scheme 7.

DISCUSSION

The reactions of Scheme 7 show a sharp contrast in the behaviour of $NaBH_4$ under anhydrous and aqueous conditions. In anhydrous THF, *one mole* of sodium

Scheme 7:



$$\underset{\mathbf{1}}{[\text{CpRe(CO)}_2\text{(NO)}]^+} + 1\text{NaBH}_4 \xrightarrow[\text{25°, 60 min}]{\text{THF}} \underset{\mathbf{4}}{\text{CpRe(CO)(NO)CH}_3} \ (95\%) \tag{13}$$

$$\underset{\mathbf{1}}{[\text{CpRe(CO)}_2\text{(NO)}]^+} + 1\text{NaBH}_4 \xrightarrow[\text{0° 15 min}]{\text{THF/H}_2\text{O}} \underset{\mathbf{2}}{\text{CpRe(CO)(NO)CHO}} \ (93\%) \tag{14}$$

$$\underset{\mathbf{2}}{\text{CpRe(CO)(NO)CHO}} + 1\text{NaBH}_4 \xrightarrow[\text{25°, 60 min}]{\text{THF}} \underset{\mathbf{4}}{\text{CpRe(CO)(NO)CH}_3} \ (92\%) \tag{15}$$

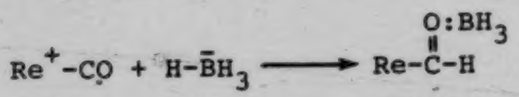
$$\underset{\mathbf{2}}{\text{CpRe(CO)(NO)CHO}} + 1\text{NaBH}_4 \xrightarrow[\text{0°, 15 min}]{\text{THF/H}_2\text{O}} \underset{\mathbf{3}}{\text{CpRe(CO)(NO)CH}_2\text{OH}} \ (94\%) \tag{16}$$

$$\underset{\mathbf{3}}{\text{CpRe(CO)(NO)CH}_2\text{OH}} + 1\text{NaBH}_4 \xrightarrow[\text{25°/ 5 hr}]{\text{THF}} \underset{\mathbf{4}}{\text{CpRe(CO)(NO)CH}_3} \ (97\%) \tag{17}$$

$$\underset{\mathbf{3}}{\text{CpRe(CO)(NO)CH}_2\text{OH}} + 1\text{NaBH}_4 \xrightarrow[\text{25°/ 5 hr}]{\text{THF/H}_2\text{O}} \underset{\mathbf{4}}{\text{CpRe(CO)(NO)CH}_3} \ (88\%) \tag{18}$$

borohydride is capable of reducing coordinated carbon monoxide, formyl or hydroxymethyl ligands to a methyl group. In the presence of water each of these reactions proceeds only to the next more reduced state.

(1) Reduction of coordinated CO. Under anhydrous conditions [Eq (13)] one mole of $NaBH_4$ reduces coordinated carbon monoxide to the methyl group. However, in aqueous solution this same reaction proceeds only to the formyl stage [Eq (14)]. The first step in both these reactions probably involves a one hydride transfer [Eq (19)] giving the formyl perhaps as a borane adduct.



$$Re^{+}-CO + H-\bar{B}H_3 \longrightarrow Re-\overset{O:BH_3}{\overset{\|}{C}}-H \qquad (19)$$

1 **2a**

In aqueous solution borane would undergo rapid hydrolysis* to boric acid preventing further reduction [Eq (14)] and allowing isolation of formyl **2**.

Eq (13) suggests that in anhydrous THF the initial formyl-BH_3 adduct **2a** rearranges to give ultimately the methyl derivative **4**. The borane reduction of formyl **2**, is similar to the reaction of metal acyls, $M-\overset{O}{\overset{\|}{C}}-CH_3$ with $BH_3 \cdot THF$ first reported by Masters[46] in 1976. A mechanism [Eq (20)] was suggested involving initial formation of an acyl-BH_3 adduct (viii), which rearranges to the borane ester (ix). Masters postulated

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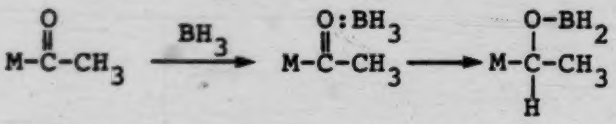
*This is consistent with the observation that the aqueous reactions of Eq (14), (16) and (18) occur with gas evolution, presumably hydrogen.

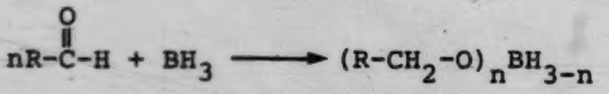


$$M-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{BH_3} M-\overset{O:BH_3}{\overset{\|}{C}}-CH_3 \longrightarrow M-\underset{H}{\overset{O-BH_2}{C}}-CH_3 \qquad (20)$$

(viii) (ix)

the borane ester (ix) is attacked by a *second mole* of BH_3 to give the ethyl complex $M-CH_2-CH_3$ and $[BH_2OBH_2]$. Obviously the stoichiometry and yield of Eq (13) rule out this type of mechanism for the BH_3 reduction of the formyl **2**.

Borane has been used extensively in organic chemistry to reduce aldehydes.[47] The initial step again involves formation of a BH_3 carbonyl adduct. With aldehydes this adduct undergoes further reaction to give various borane esters [Eq (21)].



$$nR-\overset{O}{\overset{\|}{C}}-H + BH_3 \longrightarrow (R-CH_2-O)_nBH_{3-n} \qquad (21)$$

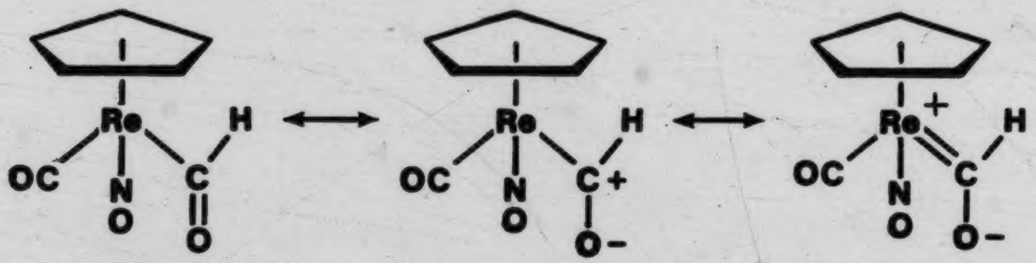
(x)

n = 1, 2 or 3.

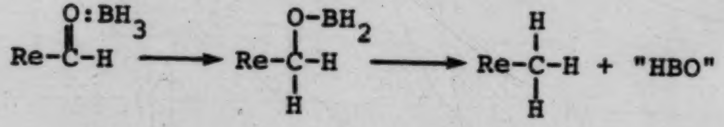
However, this reaction does not proceed to the alkane $R-CH_3$; rather, hydrolysis of (x) is required giving the alcohol $R-CH_2OH$. Neither of these mechanisms satisfactorily explains generation of the methyl **4** in Eq (13).

The resonance forms of $(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$ (2) (Scheme 8) show a high electron density on oxygen, suggesting the formyl complex should be a good Lewis base.

Scheme 8:



After the initial hydride transfer from BH_4^- in Eq (13), the formyl may exist as an adduct 2a with the Lewis acid BH_3. Hydride transfer as in the reduction of organic aldehydes would give a borane ester [Eq (22)].



$$\mathrm{Re{-}\overset{\overset{O:BH_3}{\|}}{C}{-}H} \longrightarrow \mathrm{Re{-}\underset{\underset{H}{|}}{\overset{\overset{O{-}BH_2}{|}}{C}}{-}H} \longrightarrow \mathrm{Re{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H} + \text{"HBO"} \qquad (22)$$

2a   2b

However, unlike the reduction of organic aldehydes the borane ester 2b, Eq (22), apparently eliminates HBO* to give the methyl complex 4.

---

*HBO represents one unit of trimeric boroxine, $(HBO)_3$ which is unstable with respect to diborane and boric oxide.[48]

These reactions [Eqs (13, 14)] provide a remarkable example of activation of a ligand on coordination to a transition metal. Sodium borohydride will not reduce carbon monoxide under ordinary conditions[49] and yet reduction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ occurs rapidly at room temperature. Activation in this case, consists of increased positive charge on the carbonyl carbon due to electron donation to rhenium. Increased electrophilic character of the CO ligand promotes hydridic reduction.

(2) Reduction of coordinated formyl. As shown in Scheme 7 *one mole* of $NaBH_4$ reduces the formyl ligand to hydroxymethyl in aqueous solution [Eq (15)] or to methyl [Eq (16)] in anhydrous THF. It is informative to compare the formyl reactions with borohydride reduction of an organic aldehyde.

Sodium borohydride reacts[47] with *four moles* of aldehyde as shown in Eq (23).

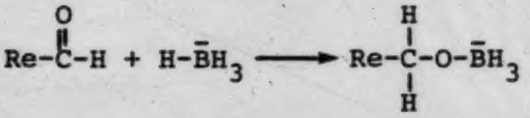
$$4R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H + 1NaBH_4 \longrightarrow (R\text{-}CH_2\text{-}O)_4BNa \qquad (23)$$

This reaction occurs with four successive hydride transfers each faster than the previous step. This observation is consistent with the greater hydride donating ability of alkoxyboranes as compared to borane itself. When this reaction is carried out under aqueous conditions the product $NaB(O\text{-}CH_2\text{-}R)_4$ is hydrolyzed to the alcohol

RCH_2-OH and $NaB(OH)_4$.

In contrast to organic aldehydes, the formyl complex **2** consumes *1 mole* of $NaBH_4$. In the presence of water the hydroxymethyl species **3** is formed, under anhydrous conditions the reduction continues to the methyl **4**. The use of less than one mole of $NaBH_4$ results in incomplete reaction.* Obviously the $NaBH_4$ reduction of aldehydes and transition metal formyls do not occur in the same manner.

As suggested by the resonance structure of Scheme 8 the formyl complex **2** should be susceptible to nucleophilic attack at the -CHO carbon. A reasonable first step in the reactions of both Eq (15) and (16) is hydride attack at the formyl ligand as shown in Eq (24).



$$\mathrm{Re{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}H} + \mathrm{H{-}}\overset{-}{\mathrm{B}}\mathrm{H_3} \longrightarrow \mathrm{Re{-}}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{\mathrm{C}}}\mathrm{{-}O{-}}\overset{-}{\mathrm{B}}\mathrm{H_3} \qquad (24)$$

2c

In the presence of water the alkoxyborohydride **2c** must be hydrolyzed to the hydroxymethyl complex **3**. This hydrolysis occurs at a rate faster than **2c** can reduce a second mole of formyl. Perhaps the great bulk of the rhenium group prevents the formation of a dialkoxyborohydride species. Under anhydrous conditions [Eq (15)] the alkoxyborohydride $\underset{\sim}{2c}$ must rearrange to the methyl complex $\underset{\sim}{4}$. It is difficult to imagine a mechanism for such a transformation. The reaction of Eqs (15) and (16) demonstrate the behavioural modification often observed on coordination of a functional group to a transition metal; one of the more interesting and useful aspects of organotransition metal chemistry.

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*This difference in stoichiometry is further emphasized by Eq (16). If 4 moles of the rhenium formyl had reacted with $NaBH_4$ the resulting $-CH_2-OH$ complex would have been further reduced to the methyl as shown in Eq (18).

(3) Reduction of Coordinated Hydroxymethyl. The reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ ($\underset{\sim}{3}$) with *one mole* of $NaBH_4$ gives under anhydrous or aqueous conditions the methyl complex $\underset{\sim}{4}$ (Scheme 7). The reactions of Eqs (17) and (18) again show the contrast between organic functional group chemistry and organotransitional metal chemistry. Alcohols are not generally reduced by sodium borohydride.[47] Certain acidic alcohols,[50] such as methanol do react with $NaBH_4$ [Eq (25)]; but these reactions occur with deprotonation not reduction of the alcohol.

$$NaBH_4 + MeOH \xrightarrow{60°C} [CH_3\text{-}O\text{-}BH_3]Na + H_2 \qquad (25)$$

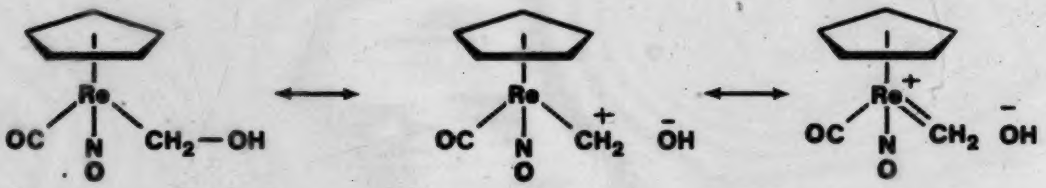
Upon coordination to the rhenium group the $\text{-}CH_2\text{-}OH$ group readily undergoes hydroxide displacement with

$NaBH_4$. This reaction probably involves a nucleophilic attack by H^- to displace OH^- [Eq(26)]. This remarkable change in reactivity from that of organic alcohols is

$$\text{Re-CH}_2\text{OH} + 1\text{NaBH}_4 \longrightarrow \text{Re-CH}_3 + \text{NaH}_3\text{B(OH)} \qquad (26)$$

readily rationalized in terms of the resonance forms of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ (Scheme 9).

Scheme 9:



Coordination of $-CH_2OH$ to rhenium greatly enhances the partial positive charge on the methylene carbon. A coordinated-CH_2 carbene species, $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)CH_2]$-$BF_4$ has been prepared in a recent study.[51] This complex is readily attacked by hydride sources to form the methyl complex 4. The presence of the rhenium group has activated the hydroxymethyl ligand towards reduction by hydridic reagents.

* * * * * *

A careful study of the reactions of $NaBH_4$ with $[(\eta-C_5H_5)Re(CO)_2(NO)]^+$ ($\underset{\sim}{1}$) has resulted in isolation of complexes containing coordinated formyl, hydroxymethyl and methyl ligands. It has been shown that coordinated carbon monoxide $[M-CO]^+$ can be reduced as shown in Eq (8) through M-CHO and $M-CH_2OH$ stages to give $M-CH_3$. However, previous suggestions[33,12] that formyl and hydroxymethyl derivatives are intermediates in the three step sodium borohydride reduction of $[M-CO]^+$ to $M-CH_3$ under *anhydrous conditions* are imprecise in an important respect. Such intermediates are most probably present as borane adducts or esters [Eq (22)], differing from the "free" formyl or hydroxymethyl compounds which are obtained upon hydrolysis. Thus, it is noted that the rate of reaction of pure $(\eta-C_5H_5)Re(CO)(NO)CH_2OH$ ($\underset{\sim}{3}$) in THF (Scheme 7 , Eq (17)) is qualitatively much slower than the reduction of cation $\underset{\sim}{1}$ to the methyl derivative $\underset{\sim}{4}$ [Eq (13)]; hence the hydroxymethyl complex $\underset{\sim}{3}$ as such cannot be an intermediate in the overall reduction of Eq (13).

D. Further Comments on the Mechanism of the Fischer-Tropsch Synthesis.

The studies on the reactions of $[(\eta-C_5H_5)Re(CO)_2(NO)]^+$ with $NaBH_4$ show that coordinated carbon monoxide can be reduced through formyl and hydroxymethyl stages to a methyl group. These results confirm that the mechanism for the Fischer-Tropsch Synthesis described in Section I-B has invoked reasonable intermediates for CO reduction. However, as might be expected from an area of such intense study, current views as to the mechanism of the Fischer-Tropsch synthesis have undergone many changes since the beginning of the present study.

Recently, some workers[29] have expressed doubts as to the existence of a simple metal formyl intermediate in the catalytic reduction of carbon monoxide. The first step of Scheme 4 , insertion of CO into a metal hydride bond has been questioned due to lack of a clear example in organotransition metal chemistry to date. This is particularly surprising since the corresponding insertion of CO into metal carbon bonds is a well known and thoroughly studied process.[52] Further discussion on this subject is beyond the scope of the present work. The reader is referred to a recent review by Masters,[29] although cautioned that this article may already be out of date.

Whatever the role of formyl complexes in future mechanisms for Fischer-Tropsch reactions, the study of carbon monoxide reduction promises to remain an integral part of organotransition metal chemistry throughout the 1980's.

E. Studies of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ by Other Workers.

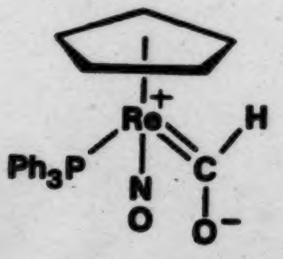
In the late 1970's many research groups were interested in the preparation of a stable, neutral transition metal formyl complex by reduction of coordinated carbon monoxide. The rhenium formyl, $(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$ (**2**) appeared to be an excellent candidate. Graham and his co-workers[12] had already shown in 1972, that the carbonyl cation, $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$, could be reduced by a hydride source. In addition, the neutral $(\eta\text{-}C_5H_5)Re(CO)(NO)X$ derivatives reported by these workers[12] showed excellent thermal stability, a prerequisite for isolation of a neutral formyl. Thus, it is not too surprising that the reduction of the rhenium cation **1** has been investigated by other research groups, in particular those of C. P. Casey at Wisconsin and J. A. Gladysz at University of California-Los Angeles.

The formyl complex **2** was reported by both Casey[53] and Gladysz[39] from reaction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (**1**) with lithium triethylborohydride. Prepared in this manner the formyl was obtained as an impure oil, due no doubt to the presence of triethylborane. Both authors explored the further reduction of the formyl complex. It was shown that reaction of **2** with $BH_3 \cdot THF$ does indeed give $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ (**4**) as suggested in Eq (22) of Section II-C. The reaction of the formyl complex **2** with

$LiHBEt_3$ surprisingly gave hydride attack at the carbonyl ligand, generating an anionic bisformyl complex,

$$(\eta\text{-}C_5H_5)Re(CO)(NO)CHO + HBEt_3^- \longrightarrow (\eta\text{-}C_5H_5)Re(NO)(CHO)_2^- + BEt_3 \qquad (27)$$

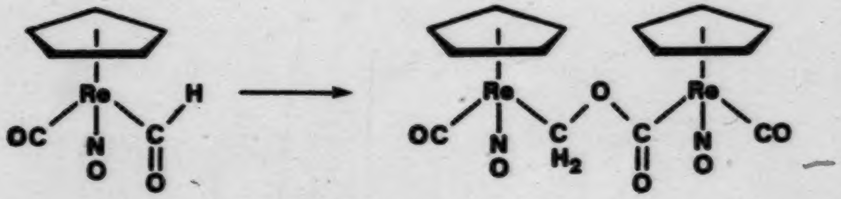
[Eq (27)]. This contrasts sharply with the reaction of **2** with $NaBH_4$ shown in Scheme 7 , wherein hydride attack occurs at the formyl ligand. Gladysz[39] reported the phosphine substituted formyl, $(\eta\text{-}C_5H_5)Re(PPh_3)(NO)CHO$ from $LiHBEt_3$ reduction of $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)]^+$. This new formyl complex showed greatly enhanced thermal stability, allowing the first X-ray study[54] of a formyl complex. The structural determination of $(\eta\text{-}C_5H_5)Re(PPh_3)$-(NO)CHO, showed an unusually short Re-C formyl bond, suggesting significant contribution from the carbene



xi

canonical form (xi).

Casey reported[55] a study on the decomposition products of 2. As stated in Section II-B, the formyl complex decarbonylates in dilute solutions to give $(\eta\text{-}C_5H_5)Re(CO)(NO)H$. However, as a neat oil the formyl undergoes a condensation reaction giving a dimeric metalloester [Eq (28)]. Hydrolysis of this metalloester provided



(28)

Casey with a route (albeit a difficult one) to the hydroxymethyl species, $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_2OH$ (3).

SECTION III

THE REDUCTION OF COORDINATED CARBON MONOXIDE TO THE HYDROXYCARBONYL LIGAND

A. Introduction

As outlined in Section I-A, hydroxycarbonyl complexes have recently attracted much interest as possible intermediates in the Water-Gas Shift reaction. Despite intense study, few examples of stable, isolable compounds have yet been found. The first mention of a metal complex containing the -COOH ligand comes from the early work of Hieber[56] in 1933. Alkali treatment of iron pentacarbonyl solutions were reported to give CO_2 evolution and the corresponding hydride anion [Eq (29)]. Hieber postulated that hydride production occurred by decarboxylation of an hydroxycarbonyl intermediate. This method has since been used to prepare a number of transition metal hydrides.[57]

$$Fe(CO)_5 + OH^- \longrightarrow [(OC)_4FeCOOH]^- \longrightarrow HFe(CO)_4^- + CO_2 \qquad (29)$$

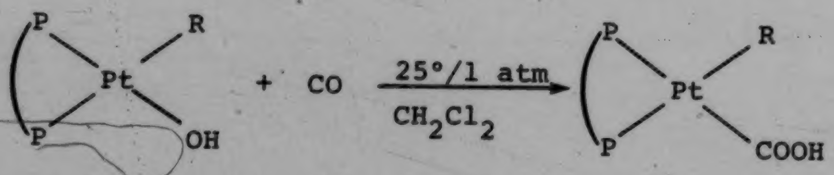
The first stable hydroxymethyl complex (or metallocarboxylic acid) was obtained by reduction of coordinated carbon monoxide with water. In 1969, Deeming and Shaw[58] reported the reactions shown in Eq (30). This work first demonstrated what now appears to be a general reaction

$$\mathrm{Ir(L)_2Cl_2(CO)_2^+ + H_2O \underset{HCl/CHCl_3}{\overset{Et_2O}{\rightleftarrows}} Ir(L)_2Cl_2(CO)COOH} \quad (30)$$

$L = PMe_2Ph, AsMe_2Ph$

of metallocarboxylic acids. Upon acidification, water is lost to regenerate the corresponding carbonyl ($MCOOH + H^+ \rightarrow M\text{-}CO^+ + H_2O$). In agreement with Hieber's postulated mechanism, the new complexes readily decarboxylated, thermally to give the iridium hydrides, $Ir(L)_2Cl_2(CO)H$.

At the time of the present work, the only other stable hydroxycarbonyl was a platinum complex reported in 1973 by Appleton and Bennett[59] [Eq (31)].



(31)

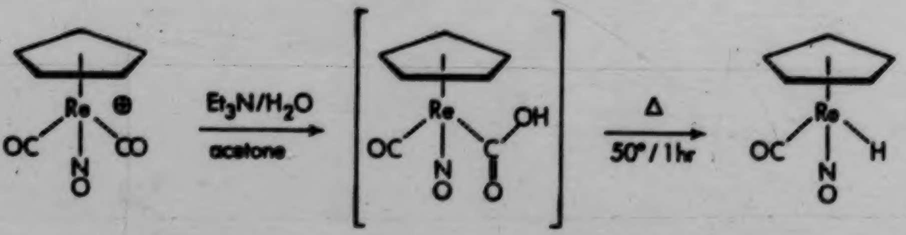
P-P = 1,2-bis(diphenylphosphino)ethane or "diphos"

R = CH_3, cyclohexenyl.

This interesting reaction appears to involve carbonyl insertion into a Pt-O bond under extremely mild conditions.

In 1972, $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$) was prepared by this research group.[12] The hydride was obtained on treatment of the cationic carbonyl $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ ($\underset{\sim}{1}$) with base in acetone followed by a 1 hr reflux.

The authors postulated the intermediacy of a metallocarboxylic acid, (η-C_5H_5)Re(CO)(NO)COOH ($\underset{\sim}{6}$), although they did not attempt to isolate such a compound [Eq (32)].



(32)

The present interest in transition metal hydroxycarbonyl species prompted a reinvestigation of this reaction. The known properties[12] of (η-C_5H_5)Re(CO)(NO)X derivatives suggested $\underset{\sim}{6}$ if it could be isolated, might show good thermal stability. The results of this study are described in the following section.

B. Results and Discussion

(1) Preparation of (η-C_5H_5)Re(CO)(NO)H ($\underset{\sim}{5}$). The original preparation[12] of (η-C_5H_5)Re(CO)(NO)H ($\underset{\sim}{5}$) gave the hydride as an orange oil in 60% yield. On repeating this reaction with careful product recovery it was possible to increase the yield to 93%. Very slow cooling of a saturated pentane solution gave the hydride $\underset{\sim}{5}$ as orange, air stable *crystals*. The very low melting point (30.5-31°C) of the hydride accounts for its

original report as a liquid. The hydride was identified by comparison of its infrared, proton NMR and mass spectra to literature values.[12] The proton NMR shows a characteristic[60] transition metal hydride peak at -8.50 ppm. It was of interest to determine the Re-H stretching frequency. Although no suitable band was observed in the infrared, the Raman spectrum of 5 shows a peak at 2050 cm^{-1} tentatively assigned to ν(Re-H). This was confirmed by preparation* of $(\eta\text{-}C_5H_5)Re(CO)(NO)D$ (7) which showed ν(Re-D) at 1465 cm^{-1} (ν(Re-H)/ν(Re-D) = 1.41). The remarkable thermal stability of 5 suggests an unusually high Re-H bond strength. This is certainly not reflected in the value of ν(Re-H), which is similar to other transition metal hydrides,[61] some of much lower stability.

The properties and reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) are further discussed in Chapter III.

(2) Preparation and Reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$ (6).

When $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) was prepared as described in the Experimental, it was noted that addition of Et_3N to a yellow solution of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (1) in acetone/H_2O produced an orange color. If the reaction is stopped at this stage no hydride can be recovered. It was felt that this orange color might be due to an hydroxycarbonyl species, which in excess base would exist as the carboxylate anion. To isolate $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$ (6) it would be necessary to avoid excess base. This was accomplished by adding base (Et_3N or NaOH) to $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ in *aqueous* solution. As the hydroxycarbonyl forms it precipitates* as analytically pure, yellow microcrystals.

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*$(\eta\text{-}C_5H_5)Re(CO)(NO)D$ (7) was obtained using the procedure for the preparation of the hydride 5 in D_2O/acetone-d_6.

The metallocarboxylic acid 6, shows good air and thermal stability, slowly decomposing at ~90°C. The compound was identified by elemental analysis, and infrared, proton NMR and mass spectra. The ν(OH) and ν(COOH) stretching frequencies were located at 2960 (br,s) and 1631 (m) cm^{-1}, respectively. The proton NMR shows a broad peak at 9.47 ppm (CD_2Cl_2) assigned to the -COOH proton. The acid proton readily exchanges with added D_2O.

The reaction of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ (1) with base is very similar to its reduction with $NaBH_4$, discussed in Section III-C. Both reactions occur with reduction of coordinated carbon monoxide by nucleophilic attack on the carbonyl carbon. This process is assisted by creation of a positive charge at carbon, due to coordination to the rhenium group. If one CO ligand of 1, is replaced by a phosphine,* the resulting cations are resistant to base attack. The greater sigma donor ability of phosphines promotes more back donation to the remaining CO of $[(\eta\text{-}C_5H_5)Re(L)(CO)(NO)]^+$ reducing the partial positive charge at carbon and preventing nucleophilic attack by OH^-. Similar behaviour has recently been reported by Pettit[62] for the bisphosphine complex $[(\eta\text{-}C_5H_5)Fe(L_2)(CO)]^+$; L_2 = diphos.

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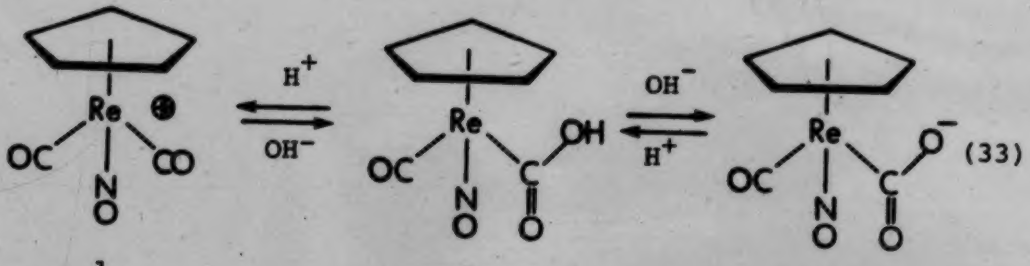
*If one continues to add excess base in this reaction, 6 redissolves to give a red solution, presumably of the carboxylate anion.

The reactions of 6 are characterized by its amphoteric nature as shown in [Eq (33)].



1 6 6a

The addition of Et_3N to D_2O/acetone-d_6 solution results in the disappearance of the peak at 5.96 for 6 and the appearance of a new $(\eta\text{-}C_5H_5)$ peak at 5.76 ppm assigned to the carboxylate anion* (6a). In the presence of strong acids like HBF_4/Et_2O, $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$ (6) is protonated to regenerate the carbonyl cation 1. The amphoteric properties of metallocarboxylic acids have recently been explored by Pettit[62] with $(\eta\text{-}C_5H_5)\text{-}Fe(L)_2COOH$, (L = CO, phosphines) derivatives.

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*Preparation of the phosphine cations, $[(\eta\text{-}C_5H_5)Re(L)(CO)\text{-}(NO)]^+$; L = PPh_3, $P(CH_3)_2Ph$ is described in Chapter III.

(3) Decarboxylation studies on $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$ (6). Once the hydroxycarbonyl 6 had been isolated it was possible to test its intermediacy[12] in the preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5). When $(\eta\text{-}C_5H_5)\text{-}Re(CO)(NO)COOH$ (6) is subjected to the conditions of the hydride preparation, it reacts to give only $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (>90% yield). This is consistent with formation of 5 by thermal decarboxylation of the hydroxycarbonyl. However, if 6 is heated in acetone/H_2O (no Et_3N) for 1.5 hrs, only traces of 5 are formed. This suggests decarboxylation occurs not from 6, but rather by CO_2 loss from the corresponding carboxylate anion 6a. The original mechanism proposed by Graham, *et al.*[12] should include a deprotonation step [Eq (34)].

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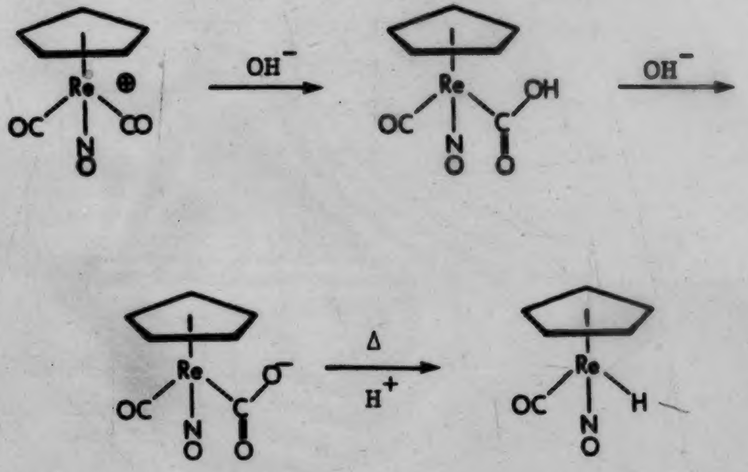
*No attempts were made to isolate the carboxylate anion.



(34)

These results contrast sharply with those recently reported by Pettit[62] for the hydroxycarbonyl $(\eta\text{-}C_5H_5)\text{-}Fe(CO)(PPh_3)COOH$. It was found that the iron metallocarboxylic acid rapidly loses CO_2 on heating, while the corresponding potassium salt was stable to 100°C. It is not immediately obvious what factors determine this difference in the route of decarboxylation for the iron and rhenium compounds.

* * * * *

Metallocarboxylic acids have been postulated as reaction intermediates* for nearly 50 years, and yet until 1969 no stable examples were known. This could have implied an inherent instability of the M-COOH moeity. The work discussed above suggests that lack of metallocarboxylic acids is due not to an inherent weakness of the metal carbon bond; rather as with metal formyl complexes it is because of a low energy pathway to rearrangement. In the case of hydroxycarbonyl complexes this pathway is facile decarboxylation.

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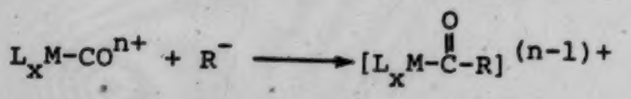
*In addition to the Water-Gas Shift reaction, metallocarboxylic acids have been invoked as intermediates in a number of catalytic and stoichiometric reactions. For a recent discussion see reference 29.

SECTION IV

REACTIONS OF $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ WITH OTHER NUCLEOPHILES

A. Introduction

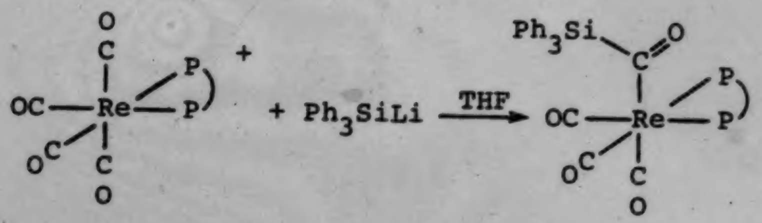
Some of the earliest examples[63] of reduction of coordinated carbon monoxide were provided by reaction of metal carbonyls with alkyl anions [Eq (35)].



$$L_xM\text{-}CO^{n+} + R^- \longrightarrow [L_xM\text{-}\overset{O}{\overset{\|}{C}}\text{-}R]^{(n-1)+} \qquad (35)$$

This very general reaction involves the addition of a carbanion to a CO ligand at carbon which, relative to oxygen is the more positively charged site. If the starting metal carbonyl is cationic (n = 1), the product is a neutral acyl complex, $L_xM\text{-}\overset{O}{C}\text{-}R$. Neutral carbonyl substrates (n = 0), give acylate anions, $[L_xM\text{-}\overset{O}{C}\text{-}R]^-$, which are precursors to carbene complexes.[64]

An interesting extension of Eq (35), was reported in 1976 by Graham and co-workers.[65] This study produced the first transition metal silyacyls [Eq (36)]. This



(36)

P—P = diphos.

particular rhenium cation was chosen for the known stability of its derivatives. Even so, reactions with other group IVA anions (Ph_3Ge^-, Ph_3Sn^-) gave only the decarbonylation products, Re(diphos)$(CO)_3EPh_3$ (E = Ge, Sn).[66]

Transition metal acyl complexes are important intermediates in a variety of reactions, and as such they have received much study.[52,67] Recently, renewed interest in acyls has arisen due to their use as models for chain extension steps (see Scheme 4) in hydrocarbon production with transition metal catalysts. The availability of a suitable carbonyl cation, $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ ($\underset{\sim}{1}$) provided an opportunity to explore the above reactions. It was hoped that the high thermal stability of $(\eta\text{-}C_5H_5)Re(CO)(NO)X$ species would allow isolation of a variety of group IVA acyls.

B. Results and Discussion

Addition of methyllithium to a THF suspension of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+BF_4$ ($\underset{\sim}{1}$) at -78°C gave a dark red solution from which could be isolated, by chromatography, the methyl acyl $(\eta\text{-}C_5H_5)Re(CO)(NO)C(O)CH_3$ ($\underset{\sim}{8}$). The complex formed as yellow, air and thermally stable crystals in 31% yield. The acyl was characterized by infrared, proton NMR and mass spectroscopy. The IR shows a band at 1628 cm^{-1} (hexane) typical of transition metal acyls. No evidence was found in this reaction for the methyl complex 4, the decarbonylation product of 8. This suggests that the relatively low yield of 8 was due to difficulties encountered in carrying out the reaction and in product recovery; not decomposition of the acyl.

A silyacyl derivative, if it could be formed and isolated, might be expected to show similar stability to that of 8. However, in numerous attempts to prepare $(\eta\text{-}C_5H_5)Re(CO)(NO)C(O)SiPh_3$ from reaction of Ph_3SiLi with 1, only spectroscopic evidence for the silyacyl was obtained (IR (THF)): 1986(s), 1729(s), 1633(m). Proton NMR (THF-d_8) 5.25(s), 7.3(m) ppm . If the silyacyl was formed in this reaction it did not decarbonylate to $(\eta\text{-}C_5H_5)Re(CO)(NO)SiPh_3$. All attempts to purify the compound resulted in decomposition to non-carbonyl containing products.

SECTION V

EXPERIMENTAL

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Chromatography was performed under a nitrogen blanket with degassed solvents and supports. Most of the compounds prepared in this work do show oxygen sensitivity, particularly in solution; however all can be handled for brief periods in the air.

Solvents were distilled under nitrogen from the following drying agents: pentanes, hexanes and benzene from CaH_2; CH_2Cl_2 and acetonitrile from P_2O_5; THF from potassium/benzophenone; nitromethane from $CaCl_2$; acetone from Drierite; anhydrous ether was used as obtained from Mallinckrodt Chemical Works.

$(\eta\text{-}C_5H_5)Re(CO)_3$ was prepared by literature methods.[68] All other reagents were purchased from commercial suppliers and used as obtained.

Infrared spectra were recorded using a Nicolet MX-1 FT IR Spectrometer in 0.5 mm NaCl cells unless otherwise noted. Raman spectra were obtained with a Beckman Model 700 Laser Raman Spectrometer (Krypton Laser operating at 6471 Å). Mass spectra were measured using an Associated Electronics Industries M5-12 Mass Spectrometer coupled with a Nova-3 computer employing D5-50 software. All NMR spectra were recorded unless otherwise noted at ambient temperature using Bruker WH-200 or WH-400 FT NMR. Melting points were determined using a microscope equipped with a Kofler hot stage. Microanalyses were performed by the microanalytical laboratory of this department.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)_2(NO)BF_4$.

Nitrosoniumtetrafluoroborate (0.70 g, 6.00 mmol) in 30 mL of nitromethane was added dropwise to $(\eta\text{-}C_5H_5)Re(CO)_3$ (2.00 g, 5.96 mmol) in 30 mL of CH_3NO_2 at -15°C over a period of 1 hr. The solution gradually became light yellow. The reaction was warmed to room temperature and the solvent removed under reduced pressure. The residue was dissolved in the minimum volume of acetone, decolorized with charcoal, filtered and precipitated with ether to give lemon yellow microcrystals, 2.30 g, 91% yield.

Characterization: IR (CH_2Cl_2) 2115(s), 2060(s), ν(CO); 1813(s) cm^{-1}, ν(NO). Proton NMR (CD_2Cl_2) δ 6.36 ppm. Anal. calcd for $C_7H_5ReO_3NBF_4$: C, 19.82; H, 1.19; N, 3.30. Found: C, 19.85; H, 1.15; N, 3.37.

Preparation of $(\eta-C_5H_5)Re(CO)(NO)CHO$.

A solution of $NaBH_4$ (0.045 g, 1.18 mmol) in 5 mL of H_2O was added dropwise to a stirred solution of $(\eta-C_5H_5)Re(CO)_2(NO)BF_4$ (0.5 g, 1.18 mmol) in 5 mL of H_2O at 0°C over the course of 0.5 hrs. The initial yellow solution turned orange and an orange precipitate appeared. After addition of the $NaBH_4$, the suspension was extracted with 3 x 20 mL of hexane and these initial extracts discarded.* The aqueous suspension was then extracted with additional hexane (7 x 20 mL) and the extracts combined. Cooling the hexane solution to -78°C affords the formyl complex as an orange, microcrystalline solid, 0.25 g, 62% yield.

Characterization: IR (hexane) 1999(s), ν(CO); 1731(s), ν(NO); 1630(m) cm^{-1}, ν(CHO). Proton NMR (methylcyclohexane-d_{14}) δ 5.51 (5H), 16.2 (1H) ppm.

Preparation of $(\eta-C_5H_5)Re(CO)(NO)CH_2OH$.

A solution of $NaBH_4$ (0.090 g, 2.36 mmol) in 5 mL of H_2O was added dropwise to a stirred solution of $(\eta-C_5H_5)Re(CO)_2(NO)BF_4$ (0.500 g, 1.18 mmol) in 5 mL of H_2O and 5 mL of tetrahydrofuran (THF) at 0°C. The resulting orange solution was warmed to room temperature and extracted with 3 x 7 mL of CH_2Cl_2. The addition of hexane to the combined organic layers at -40°C gave an orange solid. Recrystallization from CH_2Cl_2/hexane at -20°C gave the hydroxymethyl compound as orange crystals, 0.279 g, 70% yield, MP 95-96°C.

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*These initial extracts contain traces of $(\eta-C_5H_5)Re(CO)(NO)CH_3$ in addition to the formyl compound.

Characterization: IR (THF) 3460(s,br), ν(OH); 1953(s), ν(CO); 1695(s) cm^{-1}, ν(NO). Mass spectrum, 70°C/16 ev. $[CpRe(CO)(NO)CH_2OH]^+$, $[CpRe(NO)CH_2OH]^+$, $[CpRe(CO)CH_2OH]^+$, $[CpReCH_2OH]^+$. Proton NMR (DMSO-d_6) δ 5.88 (5H); lines of an ABX pattern ($CH_AH_BOH_X$) at 5.55 (1H), 5.15 (1H) and 3.94 (1H) ppm; $^2J_{AX}$ 6.1, $^3J_{BX}$ 5.5, $^2J_{AB}$ 9.3 Hz. Anal. calcd for $C_7H_8ReO_3N$: C, 24,85; H, 2.37; N, 4.12. Found: C, 24.85; H, 2.36; N, 3.91.

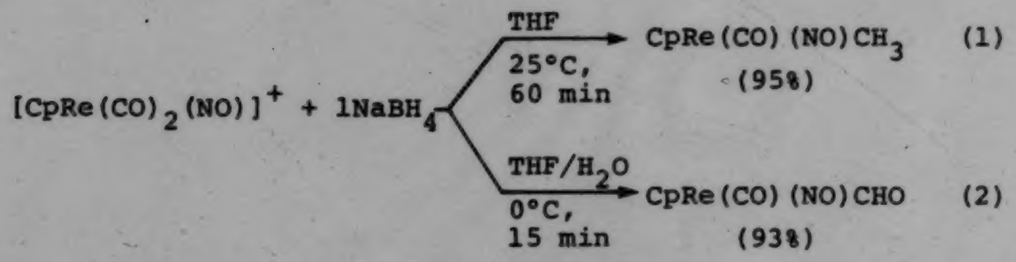
Preparation of (η-C_5H_5)Re(CO)(NO)CH_3.

A suspension of $NaBH_4$ (0.045 g, 1.18 mmol) and (η-C_5H_5)Re$(CO)_2$(NO)BF_4 (0.50 g, 1.18 mmol) in 25 mL of THF was stirred for 1.5 hrs at 25°C. The resulting red solution was filtered and the THF removed under reduced pressure. The solid residue was extracted with hexane, filtered, and slowly cooled to -40°C to give the methyl compound as red crystals, 0.336 g, 88% yield, MP 75-76°C.

Characterization: IR (hexane) 1970(s), ν(CO); 1715(s) cm^{-1}, ν(NO). Mass spectrum, 60°C/14 ev, $[CpRe(CO)(NO)CH_3]^+$, $[CpRe(NO)CH_3]^+$, $[CpReCH_3]^+$. Proton NMR (CD_2Cl_2) δ 5.62(5H), 0.92 (3H) ppm.

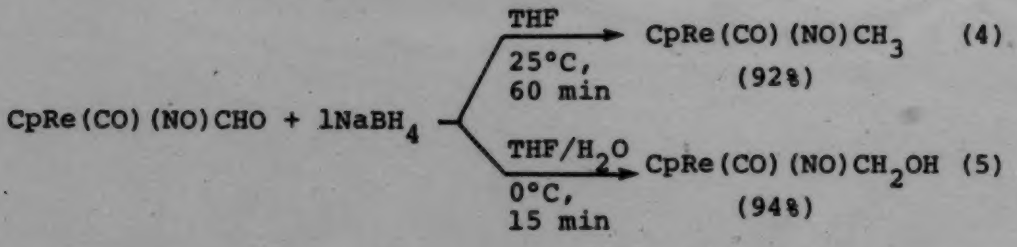
The stepwise reduction of coordinated carbon monoxide, formyl, and hydroxymethyl ligands:

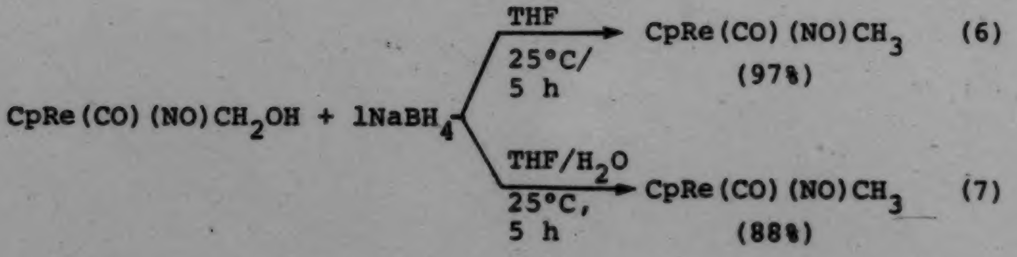
The following reactions (1) to (7) have been carried out and the yield determined by NMR as explained below.


[CpRe(CO)2(NO)]+ + 1NaBH4
THF
25°C, 60 min
CpRe(CO)(NO)CH3 (1)
(95%)
THF/H2O
0°C, 15 min
CpRe(CO)(NO)CHO (2)
(93%)

$$[\mathrm{CpRe(CO)_2(NO)}]^+ + 2\mathrm{NaBH_4} \xrightarrow[\text{0°C/ 30 min}]{\mathrm{THF/H_2O}} \mathrm{CpRe(CO)(NO)CH_2OH} \quad (3)$$

(97%)


CpRe(CO)(NO)CHO + 1NaBH4
THF
25°C, 60 min
CpRe(CO)(NO)CH3 (4)
(92%)
THF/H2O
0°C, 15 min
CpRe(CO)(NO)CH2OH (5)
(94%)


CpRe(CO)(NO)CH2OH + 1NaBH4
THF
25°C/ 5 h
CpRe(CO)(NO)CH3 (6)
(97%)
THF/H2O
25°C, 5 h
CpRe(CO)(NO)CH3 (7)
(88%)

Reactions 1 and 6:

Sodium borohydride (0.25 mmol) and the rhenium substrate (0.25 mmol) were stirred in 5 mL of THF at room temperature. When the reaction was complete, the total volume of THF was measured, an aliquot was removed and the THF evaporated from this aliquot under reduced pressure. This residue was taken up in THF-d_8, the ^1H NMR obtained, and the yield determined by integration *versus* added benzene.

Reactions 2, 3 and 7:

Sodium borohydride (0.25 mmol) in 3 mL of H_2O was added dropwise to the rhenium substrate (0.25 mmol) in 3 mL of H_2O and 3 mL of THF at the specified temperature. After the reaction was complete the solution was extracted with CH_2Cl_2, and the total volume of the extracts measured. An aliquot was removed and the solvents evaporated at -30°C under reduced pressure. The residue was dissolved in THF-d_8, the ^1H NMR obtained, and the yield calculated *versus* added benzene.

Reactions 4 and 5:

In these reactions the thermal stability of the formyl complex, $(\eta\text{-}C_5H_5)Re(CO)(NO)CHO$ required that the quantity of this reagent first be determined by ^1H NMR.

After calculating the quantity of the formyl compound present, one equivalent of $NaBH_4$ was added and the reactions and yield calculations carried out as described above.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$.

Triethylamine was added dropwise to a solution of $(\eta\text{-}C_5H_5)Re(CO)_2(NO)BF_4$ (0.50 g, 1.18 mmol) in 10 mL of water to give an orange solution with a yellow precipitate. Addition of $(C_2H_5)_3N$ was continued until precipitation was complete. The supernatant was syringed from the yellow solid which was then washed with 3 x 5 mL of H_2O and dried *in vacuo*, 0.30 g, 71%, MP 90°C (decomp.). Characterization: IR (THF) 2960(br,s), ν(OH); 1986(s), ν(CO); 1729(s), ν(NO); 1631(m) cm^{-1}, ν(COOH). Mass spectrum, 75°C/16 ev, $[CpRe(CO)(NO)COOH]^+$, $[CpRe(CO)(NO)CO]^+$, $[CpRe(CO)(NO)]^+$. Proton NMR (CD_2Cl_2) δ 5.83 (5H), 9.47 (br, 1H) ppm. Anal. calcd for $C_7H_6ReO_4N$: C, 23.73; H, 1.71. Found: C, 23.84; H. 1.69.

Protonation of $(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$.

$(\eta\text{-}C_5H_5)Re(CO)(NO)COOH$ (0.10 g, 2.82 mmol) was dissolved in 10 mL of methylene chloride giving an orange solution. The addition of HBF_4/Et_2O at 0°C gave a yellow solution from which precipitated a yellow solid. Diethyl ether (20 mL) was added to complete precipitation. The solid was collected, washed with 3 x 10 mL of ether and dried *in vacuo*. Infrared and proton NMR spectroscopy showed this material to be $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$, 0.11 g, 92% yield.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$.

Triethylamine (2.0 mL, 14.38 mmol), H_2O (2.0 mL, 111 mmol) and $(\eta\text{-}C_5H_5)Re(CO)_2(NO)BF_4$ (2.0 g, 4.71 mmol) were refluxed in 25 mL of acetone at 60°C for 1.5 hrs. The resulting red solution was extracted with 5 x 20 mL of pentane; the organic layers combined and the solvents removed under reduced pressure to give a red oil. After dissolution of the oil in the minimum volume of pentane, drying over $MgSO_4$, and filtering, cooling the solution very slowly to -78°C gave the hydride as orange crystals, 1.36 g, 93% yield, MP 30.5-31°C. Characterization: IR (hexane) 1980(s), ν(CO); 1723 (s) cm^{-1}, ν(NO). Mass spectrum, 40°C/14 ev: $[CpRe(CO)(NO)H]^+$, $[CpRe(NO)H]^+$, $[CpReH]^+$. Proton NMR (CD_2Cl_2) δ 5.60 (5H), -8.50 (1H) ppm.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)COCH_3$.

A solution of methyllithium (1.26 mmol) in Et_2O was added dropwise to a suspension of $(\eta\text{-}C_5H_5)Re(CO)_2$-$(NO)BF_4$ in 25 mL of THF at -78°C. The resulting dark red solution was warmed to room temperature and the solvents removed under reduced pressure to give a black solid. A benzene extract of this residue was chromatographed on a Silica Gel (70-230 mesh) column eluting with 1% THF/benzene. A yellow band which quickly moved down the column was collected and the solvent removed to give yellow microcrystals of the acyl compound, 0.13 g, 31% yield.

Characterization: IR (hexane) 1989(s), $\nu(CO)$; 1723(s), $\nu(NO)$; 1628(m) cm^{-1}, $\nu(COCH_3)$. Mass spectrum, 65°C/16 ev: $[CpRe(CO)(NO)COCH_3]^+$, $[CpRe(CO)(NO)CH_3]^+$, $[CpRe(CO)(NO)]^+$. Proton NMR (benzene-d_6) δ 4.85 (5H), 2.80 (3H) ppm.

CHAPTER III

THE CHEMISTRY OF (η-C_5H_5)Re(CO)(NO)H

SECTION I

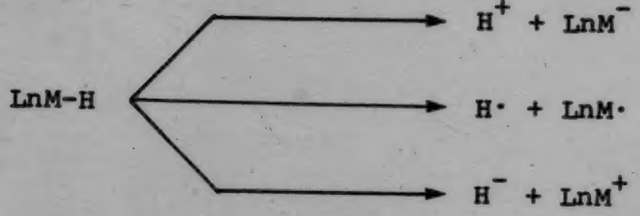
TRANSITION METAL HYDRIDES

A. Introduction

Hydride complexes of the transition metals have long occupied a central position in organometallic chemistry. Rapid development in the transition metal hydride field since the mid 1950's is due in part to their widespread application in catalytic and stoichiometric processes. Metal hydrides are intermediates in many industrial reactions such as catalytic hydrogenation of unsaturated organic molecules[69] and the Fischer-Tropsch synthesis.[70] More recently, they have shown promise as selective hydridic reducing agents.[71] In the future, metal hydrides may find use as hydrogen and energy storage systems.

Hydrides exhibit great variety in their reaction modes. The hydridic nomenclature used to describe L_nM-H species suggests such compounds will react as hydride sources. The high field ^1H NMR resonance of metal hydrides initially seemed to confirm their hydridic nature. Calculations have shown[72] localization of negative charge on the hydrogens of neutral metal carbonyl hydrides. However, for many years the most commonly observed mode of reaction for transition metal hydrides was proton loss. The carbonyl hydride, $HCo(CO)_4$, for example, acts as a strong acid in solution, with an estimated pK_a of 1.[73]

Today it is known[74] that transition metal hydrides are capable of acting as a source of protons (H^+), hydrogen atoms ($H\cdot$) or hydride ions (H^-) depending on the nature of the complex and the reaction conditions.



Scheme 10.

It is the flexible nature of the metal-hydrogen bond which is responsible for the many reaction modes reported for transition metal hydrides.

A series of comprehensive review articles[60,75] has been published in this field. Further discussion on the general area of transition metal hydride chemistry can be found in these reports.

B. Transition Metal Hydrides Containing Carbonyl and η-Cyclopentadienyl Ligands

This chapter will discuss some of the chemistry of the rhenium hydride, $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5). This compound is one of a class of hydride complexes which contain carbonyl and η-cyclopentadienyl ligands. Included in this type of complex are the Group VIb tricarbonyls and the dicarbonyls of the Iron triad.

In 1955, Fischer[76] reported the chromium group hydrides, $(\eta\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W). Wilkinson has prepared and explored the chemistry of the Group VIII hydrides $(\eta\text{-}C_5H_5)M(CO)_2H$ (M = Fe,[77] Ru[78]). Preparation of the osmium analog was only briefly mentioned in a later paper by Knox.[79] To date no other chemistry of $(\eta\text{-}C_5H_5)Os(CO)_2H$ has appeared in the literature.

The chemistry of the carbonyl-η-cyclopentadienyl hydrides shows many similarities. Thermal decomposition or oxidation leads to binuclear species [Eq (37)]. These

$$(\eta\text{-}C_5H_5)M(CO)_xH \xrightarrow[\text{or } \Delta]{[O]} [(\eta\text{-}C_5H_5)M(CO)_x]_2 \qquad (37)$$

reactions probably involve loss of H· to give the $17e^-$ metal radicals which rapidly dimerize. Resistance to thermal and oxidative decomposition increases with the atomic weight of the metal. This suggests the strength of transition metal hydride bonds may increase in descending a group of the periodic table.[75a]

The carbonyl-η-cyclopentadienyl hydrides which have been studied all act as weak acids in solution.

The corresponding carbonyl anions,[78,80] $CpM(CO)_X^-$, X = 3, 2 are well known and extremely useful reagents for the synthesis of new metal compounds. Fischer[81] has examined the proton donor ability of the chromium group tricarbonyls and estimated their acid dissociation constants to be $<10^{-5}$.

Several reactions characteristic of metal carbonyl hydrides have been reported for the above compounds. An interesting reaction occurs with diazomethane,[80,81,82] apparently involving insertion of $:CH_2$ into the metal-hydrogen bond [Eq (38)]. At 0°C in Et_2O these reactions

$$(\eta\text{-}C_5H_5)M(CO)_3H \xrightarrow{CH_2N_2} (\eta\text{-}C_5H_5)M(CO)_3CH_3 \qquad (38)$$

M = Mo, W

proceed rapidly with formation of nitrogen and the corresponding methyl compound. This provides a rather inconvenient route to these alkyl complexes which are more readily obtained from the carbonyl anions with methyl iodide.[80]

Another reaction pertinent to the present study occurs with carbonyl hydrides[83] and N-methyl-N-nitroso-p-toluenesulfonamide. Commonly known as "Diazald," this reagent often converts carbonyl metal hydrides to the nitrosyl derivative [Eq (39)]. This reaction was

$$\mathrm{LnM(H)CO} \xrightarrow{\text{Diazald}} \mathrm{LnMNO} \qquad (39)$$

reported for $(\eta\text{-}C_5H_5)Mo(CO)_3H$ by Wilkinson[80] to generate $(\eta\text{-}C_5H_5)MO(CO)_2(NO)$. A similar reaction occurs with $(\eta\text{-}C_5H_5)Fe(CO)_2H$ to give the very unstable iron nitrosyl $(\eta\text{-}C_5H_5)Fe(CO)(NO)$.[84]

Few reactions with electrophiles have yet been reported for the carbonyl-η-cyclopentadienyl hydrides. Initial electrophilic attack may be involved in a reaction common to most metal hydrides, halogenation.[85] Treatment with CX_4, X = Cl or Br to give the metal halide, has often been employed[75c] to establish the presence of a metal-hydrogen bond in newly prepared compounds. Halogenation of the $(\eta\text{-}C_5H_5)M(CO)_3H$ compounds was reported in an early paper by Wilkinson.[80] Similarly $(\eta\text{-}C_5H_5)Fe(CO)_2H$ reacts with Br_2 to give the corresponding bromide.[84]

Direct reaction of a carbonyl-η-cyclopentadienyl hydride with the electrophile H^+, was observed on protonation of $(\eta\text{-}C_5H_5)W(CO)_3H$.[86] Despite the acidic properties of the tungsten hydride, it reacts with the strong acid $CF_3COOH\text{-}BF_3\text{-}H_2O$ to give the bis-hydride cation $[(\eta\text{-}C_5H_5)W(CO)_3H_2]^+$. Protonation at the metal center was confirmed by detection of the ^{183}W satellites in the ^1H NMR.

It appears only one reaction of carbonyl-π-cyclopentadienyl metal hydrides with an organic electrophile (R^+) has been reported. This comes from the work of Beck,[87] who in 1978 reported reactions of triphenylmethyl (trityl) cation with $(\eta\text{-}C_5H_5)M(CO)_3H$ (M = Mo, W). Treatment of the tricarbonyl hydrides with $Ph_3C^+X^-$ (X = BF_4, PF_6) in CH_2Cl_2 gave triphenylmethane and metal complexes formulated as $(\eta\text{-}C_5H_5)M(CO)_3X$ [Eq (40)]. These reactions

$$(\eta\text{-}C_5H_5)M(CO)_3H + Ph_3C^+X^- \longrightarrow (\eta\text{-}C_5H_5)M(CO)_3X + Ph_3CH \qquad (40)$$

$M = Mo;\ X = BF_4,\ PF_6$

$M = W;\ X = BF_4$

occur by what must formally be considered hydride abstraction. The metal hydrides act as a source of H^- toward the electrophile Ph_3C^+.

The isolated products, $(\eta\text{-}C_5H_5)M(CO)_3{}^+$ species, appear to be coordinately and electronically unsaturated. Beck provided infrared evidence to show that, in these complexes, the ordinarily inert counter ions $BF_4{}^-$ and $PF_6{}^-$ were coordinated to the metal. This coordination presumably occurs via the fluorine atoms. At lower temperatures the reactions shown in Eq (40) were reported by Beck to give methylene chloride-stabilized species, $[(\eta\text{-}C_5H_5)M(CO)_3(CH_2Cl_2)]X$, which on warming lose CH_2Cl_2

to give the $CpM(CO)_3X$ complexes. Reaction of the $CpM(CO)_3X$ compounds with donor ligands such as Ph_3P resulted in rapid displacement of X. Similar reactions with the dicarbonyl hydrides of the iron triad have not appeared in the literature to date.

* * * * *

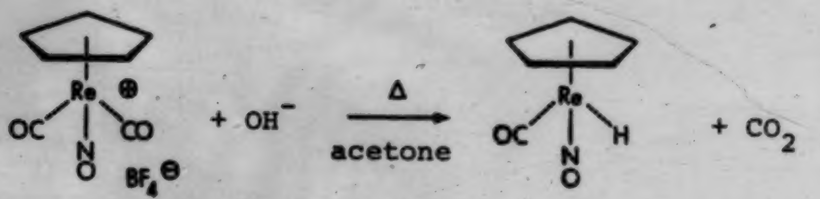
One would expect, *a priori*, the rhenium compound $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$) to exhibit behavior similar to other carbonyl-π-cyclopentadienyl hydrides. The chemistry of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ has now been thoroughly investigated and as is often the case with metal hydrides, surprising results were obtained.

SECTION II

INITIAL STUDIES ON $(\eta\text{-}C_5H_5)Re(CO)(NO)H$

A. General Properties of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$

In 1972, a new rhenium hydride, $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) was prepared in this research group.[12] The mixed carbonyl-nitrosyl hydride was obtained from treatment of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$ (1) with triethylamine-water* [Eq (41)]. In the initial report it was noted that 5 exhibited unusual behavior for a cyclopentadienyl transition metal hydride. The compound showed remarkable thermal stability. Only unreacted starting material was recovered after heating 5 at 90°C for 20 hrs. Similarly, the rhenium hydride was very resistent to oxidation. Samples have now been exposed to air for months with no signs of decomposition. The spectroscopic properties of



(41)

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*The characterization of 5 and a possible mechanism for its preparation have been discussed in Chapter II.

$(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) are comparable to those of other hydrides, thus providing no rationale for its exceptional stability.

In an attempt to better understand the nature of 5 and other CpRe(CO)(NO)-derivatives, an extensive study of its reactions has been undertaken. The results of this investigation are described in the following sections.

B. Lack of Reactivity for $(\eta\text{-}C_5H_5)Re(CO)(NO)H$

The initial obstacle in an exploration of the chemistry of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) was finding a reagent with which it would react. As discussed in Section I-B a characteristic property of transition metal hydrides of similar composition to 5, is their Lowry-Bronsted acidity. One would expect the rhenium hydride to be deprotonated in basic solution to give the anion $[(\eta\text{-}C_5H_5)Re(CO)(NO)]^-$. However, all attempts to remove H^+ from 5 with a variety of bases have been unsuccessful. The hydride is totally resistant to such reagents as triethylamine, sodium hexamethyldisilazane ($NaN[SiMe_3]_2$), potassium tert-butoxide, 1,8-bis-(dimethylamino)-naphthalene ("proton sponge") and KOH/EtOH.

Other reported reactions of transition metal carbonyl hydrides are with diazomethane to give methyl derivatives and with Diazald to give the corresponding nitrosyl. The rhenium hydride 5 does not react with either of these reagents. Treatment of 5 with CH_2N_2 in Et_2O gave no sign of $(\eta\text{-}C_5H_5)Re(CO)(NO)CH_3$ (4), even though the expected product is a very stable compound (see Chapter II). Refluxing $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with Diazald in THF showed no reaction after 48 hrs. Similar results were obtained in attempts to remove H· from 5 with various free radical sources. For example, after refluxing for 24 hrs with dibenzoylperoxide in benzene, the hydride was recovered unchanged.

The first reactions found for the rhenium hydride involved halogenation. Treatment of 5 with CBr_4 or Br_2 gives the bromide, $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9) as red, air stable crystals [Eq (42)]. The preferred route for preparation of the bromide requires refluxing 5 with Br_2 in acetone for 2 hrs (83% yield). The new complex, 9[*], was identified by infrared, proton NMR, mass spectroscopy and elemental analysis.

$$(\eta\text{-}C_5H_5)Re(CO)(NO)H \xrightarrow[\text{or } Br_2]{CBr_4} (\eta\text{-}C_5H_5)Re(CO)(NO)Br \qquad (42)$$

As discussed in Section I-B, reaction of transition metal hydrides with halogenating reagents may occur by an electrophilic mechanism. This suggested that 5 might be more reactive toward electrophiles. The following sections describe reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) with electrophiles, which formally involve hydride abstraction.

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[*] Reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9) are discussed in Chapters IV and V.

SECTION III

REACTION OF $(\eta-C_5H_5)Re(CO)(NO)H$ WITH THE ELECTROPHILE Ph_3CPF_6.

A. Preparation of the cations $[(\eta-C_5H_5)Re(CO)(NO)L]PF_6$; L = CH_3CN, THF, Acetone.

Addition of triphenylmethyl cation to a solution of $(\eta-C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$) in acetonitrile gave a 94% yield of a cationic complex formulated as $[(\eta-C_5H_5)Re(CO)(NO)(NCCH_3)]PF_6$ ($\underset{\sim}{10}$). Similar reactions between trityl cation and the hydride $\underset{\sim}{5}$ in the presence of THF and acetone gave $[(\eta-C_5H_5)Re(CO)(NO)(THF)]PF_6$ ($\underset{\sim}{11}$) and $[(\eta-C_5H_5)Re(CO)(NO)(acetone)]PF_6$ ($\underset{\sim}{12}$) in 45% and 33% yields [Eq (43)]. All three cations form as yellow, air stable

$$(\eta-C_5H_5)Re(CO)(NO)H + Ph_3C^+ \xrightarrow{L} [(\eta-C_5H_5)Re(CO)(NO)L]^+ + Ph_3CH \qquad (43)$$

L = CH_3CN, THF, Acetone

microcrystals. Their identity was established by infrared, proton NMR and elemental analysis. A comparison of the spectroscopic properties of the new compounds with those of $(\eta-C_5H_5)Re(CO)(NO)H$ is shown in Table I.

As expected, the carbonyl and nitrosyl stretching frequencies for the cations occur at higher wavenumbers than for the hydride, indicating less back-donation to

TABLE I

Comparison of IR and ^1H NMR Parameters

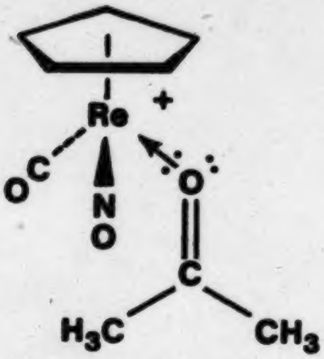
	$\nu(CO)$	$\nu(NO)$	δ(ppm)
$CpRe(CO)(NO)(NCCH_3)^+$	2030	1769	6.08(5H),2.82(1H)
$CpRe(CO)(NO)(THF)^+$	2017	1755	6.12(5H),4.24(m,4H), 2.12(m,4H)
$CpRe(CO)(NO)(acetone)^+$	2019	1757	6.16(5H),2.66(6H)
CpRe(CO)(NO)H	1971	1702	5.60(5H),-8.50(1H)

these π-acid ligands. The very high $\nu(CO)$ and $\nu(NO)$ frequencies of the acetonitrile cation relative to those of the THF and acetone complexes may indicate acetonitrile is an effective π-acid. In the ^1H NMR, the cyclopentadienyl protons were found at lower fields for the cations than for the neutral hydride $\underset{\sim}{5}$. In all $(\eta\text{-}C_5H_5)Re(CO)(NO)X$ compounds prepared in this study the IR and NMR parameters are very sensitive to the nature of the ligand X. This has proven an extremely useful aid in the preliminary identification of new compounds.

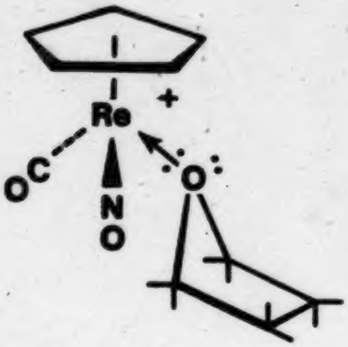
The cations $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$ (L = CH_3CN, THF, Acetone) all show proton NMR signals for L which are shifted downfield from the free ligand. This confirms that in CD_2Cl_2 (the solvent most frequently used) these ligands are coordinated to rhenium. The acetonitrile and THF cations show good stability in solution. However, the acetone cation 12 slowly decomposes in CD_2Cl_2 to give free acetone. When 12 was dissolved in acetone-d_6, the ^1H NMR immediately showed a signal for uncoordinated CH_3-C(O)CH_3. This shows that the coordinated ligand exchanges with free acetone much more rapidly than decomposition occurs.

Dissolution of the acetone cation 12 in THF, followed by precipitation with Et_2O, afforded the THF cation 11. Similarily the THF cation can be converted to 12 by stirring at room temperature in acetone. It would appear that THF and acetone are only weakly coordinated (labile) in these cations. In contrast, the acetonitrile cation 10 has shown no evidence for ligand dissociation. The presence of suitable π-acceptor orbitals on CH_3CN may account for this difference in solution properties of the cations.

Reasonable structures for the THF and acetone cations are shown as 11 and 12. These structures suggest that coordination to the rhenium group should render the two sides of the THF and acetone ligands nonequivalent. However, as shown by the ^1H NMR data of Table I this expected difference was not found. The lack of diastereotopic shifts in the THF cation 12 may be due to a rapid



11



12

inversion at the oxygen atom attached to rhenium. A fast, reversible dissociation of the coordinated ligand would equally well explain the experimental observations for both cations.

The other product obtained in the reactions shown in Eq (43) was triphenylmethane. This suggested that cation formation proceeded with hydride abstraction from 5 to give a coordinately unsaturated species $[(\eta\text{-}C_5H_5)Re(CO)(NO)]^+$ which would be rapidly attacked by the ligand L. In an attempt to better understand the mechanism of this reaction and the nature of any coordinately unsaturated intermediate(s), a thorough study of the reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with Ph_3CPF_6 in the absence of strong ligands has been undertaken.

The results of this study are described in the following sections.

B. Reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with Trityl Cation

The addition of Ph_3CPF_6 to a methylene chloride solution containing an equimolar amount of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (**5**) at 25°C resulted in a black reaction mixture from which no carbonyl containing products could be isolated. Monitoring of this reaction by ^1H NMR showed the generation of Ph_3CH and the presence of several η-cyclopentadienyl containing products. The results were much different when this same reaction was carried out at low temperature. Slow addition of trityl cation to **5** in CH_2Cl_2 at −78°C gave initially a reddish-yellow solution from which precipitated a yellow, air stable solid (**13**). The color and solubility characteristics of **13** suggested a cation of the rhenium group. The infrared spectra showed carbonyl and nitrosyl bands at 2026 and 1765 cm^{-1}, again consistent with a cationic formulation.

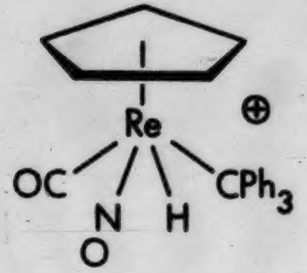
Based on the previous studies of Beck,[87] it seemed reasonable that **13** would prove to be the methylene chloride cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(CH_2Cl_2)]^+$ or a PF_6^- coordinated species, $(\eta\text{-}C_5H_5)Re(CO)(NO)(PF_6)$. However, the analysis of **13** showed high carbon and hydrogen content inconsistent with either of these structures. Repeated analyses of the new compound gave reproducible C, H and N percentages consistent with the formula $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$. The reaction of Ph_3C^+ with $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) had given a product in which the rhenium group incorporated one molecule of triphenylmethane [Eq (44)].

$$(\eta\text{-}C_5H_5)Re(CO)(NO)H + Ph_3CPF_6 \xrightarrow[CH_2Cl_2]{-78^\circ C} [(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6 \tag{44}$$

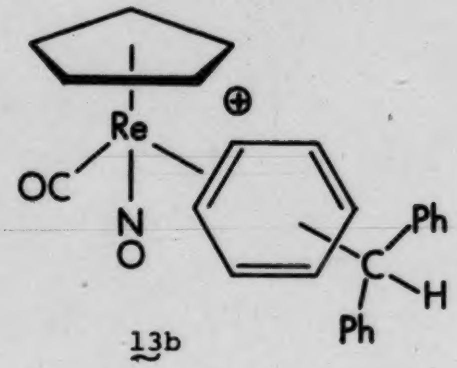
The presence of some form of triphenylmethane was confirmed by decomposition studies of 13. The complex is very unstable in solution, rapidly decomposing at *ca.* -40°C to give one mole of triphenylmethane and unidentified cyclopentadienyl products. In the solid state, 13 exhibits much higher thermal stability, only slowly decomposing at room temperature. Before discussing the ^1H NMR of 13 it is informative to examine its chemical reactions.

C. Reactions of the Triphenylmethane Cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13)

The rhenium group with a positive charge, $CpRe(CO)(NO)^+$, is a 16-electron species. To form a stable 18-electron compound this unsaturated moiety would coordinate two one-electron donors or one two-electron ligand. Keeping these electronic requirements in mind, two possible structures for the triphenylmethane cation are shown as **13**a and **13**b.



13a



13b

Both structures are consistent with the properties of **13** described in Section III-B. The hydridoalkyl **13**a would be expected to form by direct attack of trityl cation at the metal center. The η^2-arene structure **13**b could arise from initial hydride abstraction from **5**, followed by coordination of the unsaturated $CpRe(CO)(NO)^+$ to one double bond of triphenylmethane. Hydridoalkyl[88] and π-arene complexes[89] are known in organotransition metal chemistry but neither form has been reported for triphenylmethane. It was hoped that the reactions of the triphenylmethane cation **13** would provide evidence for one of these two structures.

(1) Reaction of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ with Ph_3P. The addition of one equivalent of triphenylphosphine to a CH_2Cl_2 solution of the triphenylmethane cation 13 gave a yellow solution from which was isolated a yellow, air stable solid. The new compound with the physical properties of a rhenium cation, was formulated as the triphenylphosphine complex $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3P)]PF_6$ (14) [Eq (45)] and was obtained in 96% yield.

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]^+ \xrightarrow{Ph_3P} [(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3P)]^+ + Ph_3CH \qquad (45)$$

This was confirmed by infrared, proton NMR and elemental analysis. The IR and NMR parameters of 14 are very similar to those of the acetonitrile cation 10. The new cation shows excellent thermal stability with no evidence for ligand dissociation.

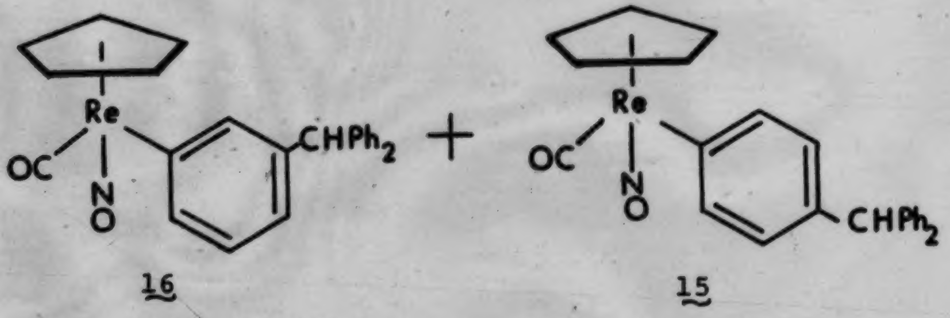
Consistent with the formulation of 13 as a triphenylmethane cation, the reaction shown in Eq (45) also produces one equivalent of Ph_3CH. Formation of the triphenylphosphine cation in this reaction could occur from either of the structures suggested for 13. In the presence of a strong ligand the hydridoalkyl structure 13a might reductively eliminate Ph_3CH, giving the coordinately unsaturated species $CpRe(CO)(NO)^+$, which would react with Ph_3P to give 14. Similarly, triphenylphosphine would be expected to displace the coordinated arene of structure 13b to give the observed products. A much more informative reaction of the triphenylmethane cation occurs with the base Et_3N.

(2) Reaction of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ with Et_3N. The two possible structures of the triphenylmethane complex would be expected to give very different products on deprotonation. The hydridoalkyl cation 13a should react with base to give a neutral triphenylmethyl complex, $(\eta\text{-}C_5H_5)(OC)(ON)ReCPh_3$, in which the trityl group is sigma bonded to rhenium through the aliphatic carbon. It was not immediately obvious what product(s) would be obtained on deprotonation of the π-arene species 13b. Coordination of a double bond to the positive metal center might activate the carbons attached to rhenium sufficiently to allow their deprotonation. This would presumably give neutral rhenium aryl derivatives.

The triphenylmethane cation 13 readily reacts with Et_3N at -78°C to give a red solution, from which can be isolated red, air stable, crystals. The infrared frequencies, color, and solubility characteristics of this material suggested a neutral CpRe(CO)(NO)- derivative. The mass spectra and analysis indicated the composition $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_{19}H_{15})$ which would be consistent with the sigma bonded triphenylmethyl compound. However, the ^{1}H NMR was much more complex than that expected for (η-C_5H_5)Re(CO)(NO)(CPh_3). In particular, two cyclopentadienyl peaks and a series of complex signals in the aromatic region were observed. It soon became evident that the deprotonation of [(η-C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6 had given *two isomeric* compounds.

The isomers were separated by repeated fractional recrystallization from hexane-dicloromethane. Each was separately characterized by infrared, proton NMR, mass spectroscopy and elemental analysis. Deprotonation of the triphenylmethane cation with triethylamine gives a mixture of para (15) and meta (16) (η-C_5H_5)(OC)(ON)Re$C_6H_4CPh_2H$ [Eq (46)].

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6 \xrightarrow{Et_3N}$$



(46)

The structures and 400 MHz proton NMR of 15 and 16 are shown in Figure II. The para isomer 15 has an

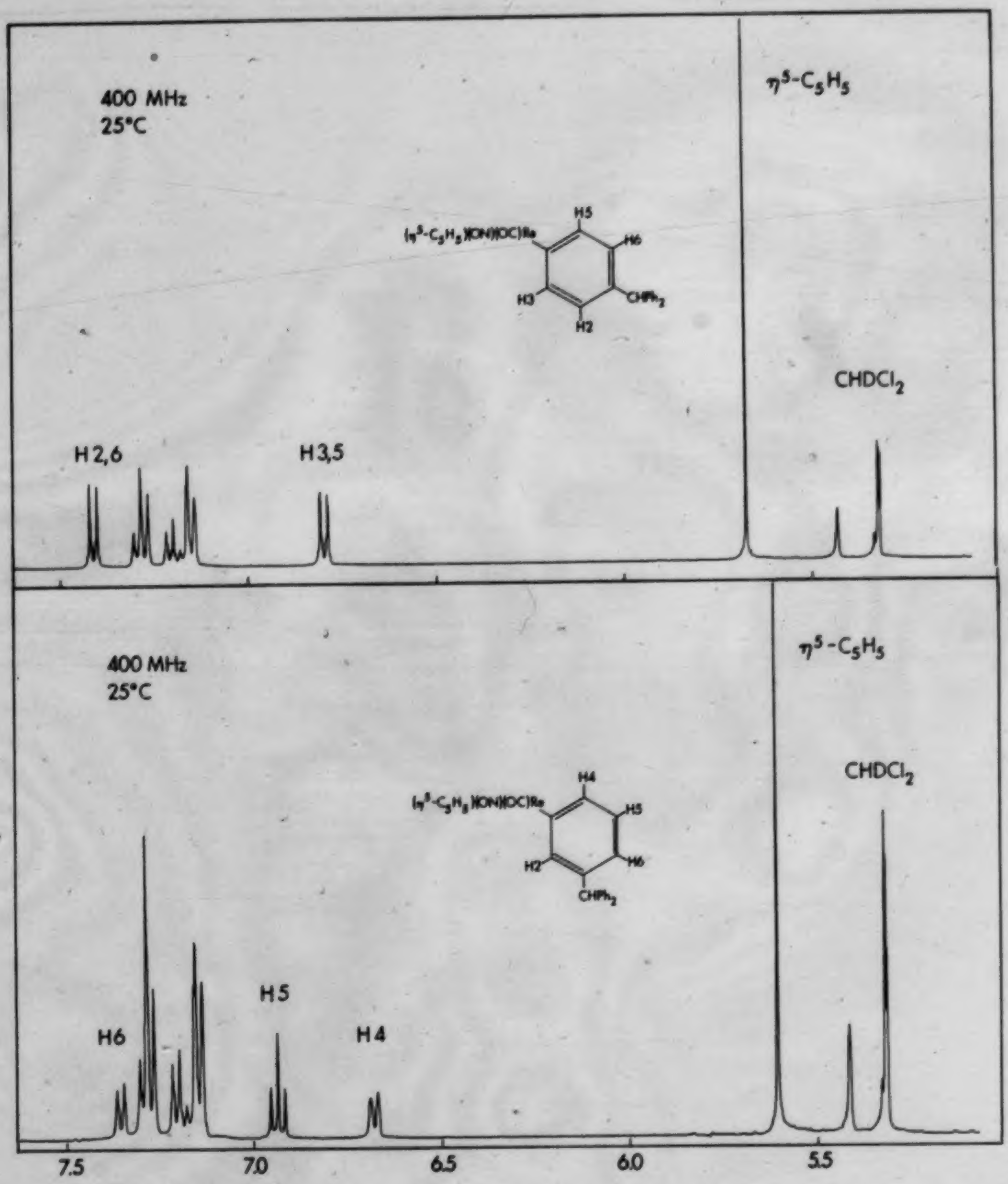


FIGURE II. ^{1}H NMR of *para* and *meta* $(\eta\text{-}C_5H_5)Re(CO)(NO)$-$(C_6H_4CPh_2H)$, 400 MHz, CD_2Cl_2.

η-cyclopentadienyl signal at 5.67 ppm (5H), a reasonable Cp shift for an aryl derivative of the rhenium group. The singlet at 5.46 δ(1H) is assigned to the aliphatic-CPh_2H hydrogen. The chemical shift of this proton has moved slightly upfield from its position (5.56 ppm) in unsubstituted triphenylmethane. In the aromatic region the monosubstituted phenyl rings occur as a series of multiplets centered at *ca.* 7.2 δ(10H). Bracketing the phenyl peaks are two doublets at 6.82 δ(2H) and 7.43 δ(2H). Decoupling the signal at 6.82δ caused collapse of the other doublet at 7.43 δ. Such an AA'XX' coupling pattern could only be consistent with para disubstitution in a C_6H_4 ring. The doublets at 6.82δ and 7.43δ have been assinged to the pairs of chemically equivalent protons H3,5 and H2,6 respectively. This assignment is based on the observation that in all the compounds prepared in this study, protons are shifted to higher fields by close proximity to the metal.

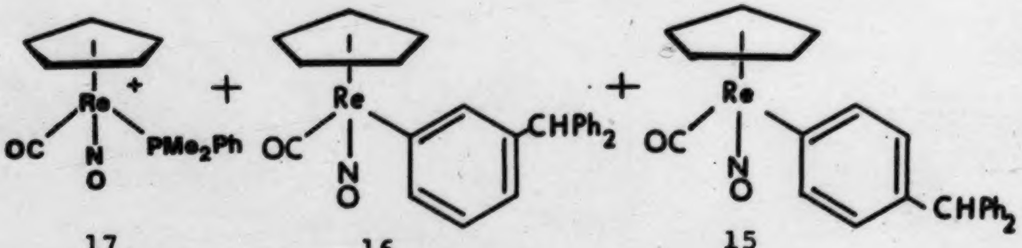
The proton NMR of the meta isomer $\underset{\sim}{16}$ (Figure II) exhibits many features similar to that of the para compound. Two singlets at 5.60 δ(5H) and 5.44 δ(1H) were assigned to the η-cyclopentadienyl and aliphatic -CPh_2H protons. In the aromatic region, it was observed that decoupling the triplet at 6.96 δ(1H), resulted in collapse of *both* doublets at 6.71 δ(1H) and 7.40 δ(1H). This coupling pattern could only be consistent with meta disubstitution. The triplet at 6.96δ was assigned to H5, coupled to both H4 and H6 ($J_{H4,H5} \simeq J_{H5,H6} = 7.3$ Hz). The doublets at 6.71δ and 7.40δ were assigned to H4 and H6, with the hydrogen closest to the metal resonating at higher field. On closer examination the signals at 6.71δ and 7.40δ were found to be triplets of doublets. This further splitting is due to meta coupling ($J_{H2,H4} \simeq J_{H2,H6} \simeq J_{H4,H6} = 1.5$ Hz). The remaining proton of the disubstituted phenyl ring, H2 is obscured by the C_6H_5 multiplets at *ca.* 7.2δ (10H).

It is noteworthy that deprotonation of the triphenylmethane cation gave only the para 15 and meta 16 compounds described above, there was no indication of an ortho isomer. The ratio of para to meta isomers in the initial product mixture before separation was 55:45. Their combined isolated yield was 89%.

Deprotonation of the triphenylmethane cation is readily reversible. Thus, treatment of a 55:45 mixture of the para 15 and meta 16 compounds with HBF_4/Et_2O at -50°C gave an 82% yield of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]BF_4$. This material was identical in every way to that obtained from treatment of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (15) with Ph_3C^+. Protonation of the para and meta compounds *separately* gave a similar result.

(3) Reaction of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ with Me_2PhP. The different products obtained in the reactions shown in Eqs 45 and 46 must be due to two competing reaction modes of the triphenylmethane cation. With the strongly coordinating ligand Ph_3P, displacement of Ph_3CH occurs, with the more basic Et_3N, the exclusive path is deprotonation of the triphenylmethane ligand. It was felt that with a suitable reagent the triphenylmethane cation might exhibit both reaction modes. Such a reaction occurs with dimethylphenylphosphine. Treatment of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ in CH_2Cl_2 with Me_2PhP gave a 2:1:1 mixture of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(PMe_2Ph)]PF_6$ (17), 15 and 16 [Eq (47)]. The new phosphine cation 17

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6 \xrightarrow{PMe_2Ph} \qquad (47)$$



17 16 15

can be isolated in 58% yield as yellow, air stable crystals. The compound was characterized by infrared, proton NMR, and elemental analysis. The ^1H NMR of 17 showed in the methyl region *two* closely spaced doublets at 2.285δ (3H) and 2.291δ (3H); $J_{(P-CH_3)}$ = 10.7 Hz. The asymmetry of the metal center in $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(PMe_2Ph)]PF_6$ renders the two methyl groups nonequivalent. The observation of this diastereotopic shift in the proton NMR confirms that the phosphine ligand is not rapidly dissociating on the NMR time scale.

The exact ratio of products obtained in Eq (47) is temperature dependent. At -78°C, the yield of the phosphine cation **17** is *ca.* 60%; at higher temperatures it drops to about 50%. The ratio of the para **15** to meta **16** isomers remains constant with temperature and is identical to that obtained with Et_3N.

The reactions of the triphenylmethane cation **13** with Et_3N and PMe_2Ph are not consistent with the hydridoalkyl structure **13a**. The products obtained in Eq (46) have arisen by deprotonation of the para and meta positions of one phenyl ring of triphenylmethane. Deprotonation of aromatic sp^2 carbons by Et_3N suggests that in the triphenylmethane cation **13**, the para and meta C-H bonds have been highly activated. Such activation would be consistent with coordination of the $CpRe(CO)(NO)^+$ group to the 3,4 double bond of one phenyl ring of triphenylmethane.

It was hoped that further evidence for this structure could be obtained from the ^1H NMR of **13**. This work is described in the following section.

D. Proton NMR Studies on $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13)

The insolubility and low thermal stability of the triphenylmethane cation 13 severely hampered attempts to obtain high quality ^1H NMR data. Extremely long acquisition times were required to collect good spectra because of the very low solubility of 13 in CD_2Cl_2. Better results were obtained in much less time by reacting trityl cation with $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) in the NMR tube. This generated supersaturated solutions, which only slowly precipitate 13. Spectra recorded in this manner were identical in every respect to those obtained on dissolution of solid samples of the triphenylmethane cation 13.

A typical 400 MHz ^1H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(Ph_3CH)]PF_6$ is shown in Figure III. The spectrum remained constant over the limited temperature range -70°C to -40°C, above which decomposition began. The triphenylmethane cation 13 shows an η-cyclopentadienyl peak at 5.90δ (5H), typical of a cation of the rhenium group. The aromatic region contains a series of complex multiplets integrating to 15 protons. These portions of the spectrum are consistent with either of the postulated structures for $[(\eta\text{-}C_5H_6)Re(CO)(NO)(Ph_3CH)]PF_6$. It is the singlet at 5.65δ (1H) which distinguishes these structures and rules

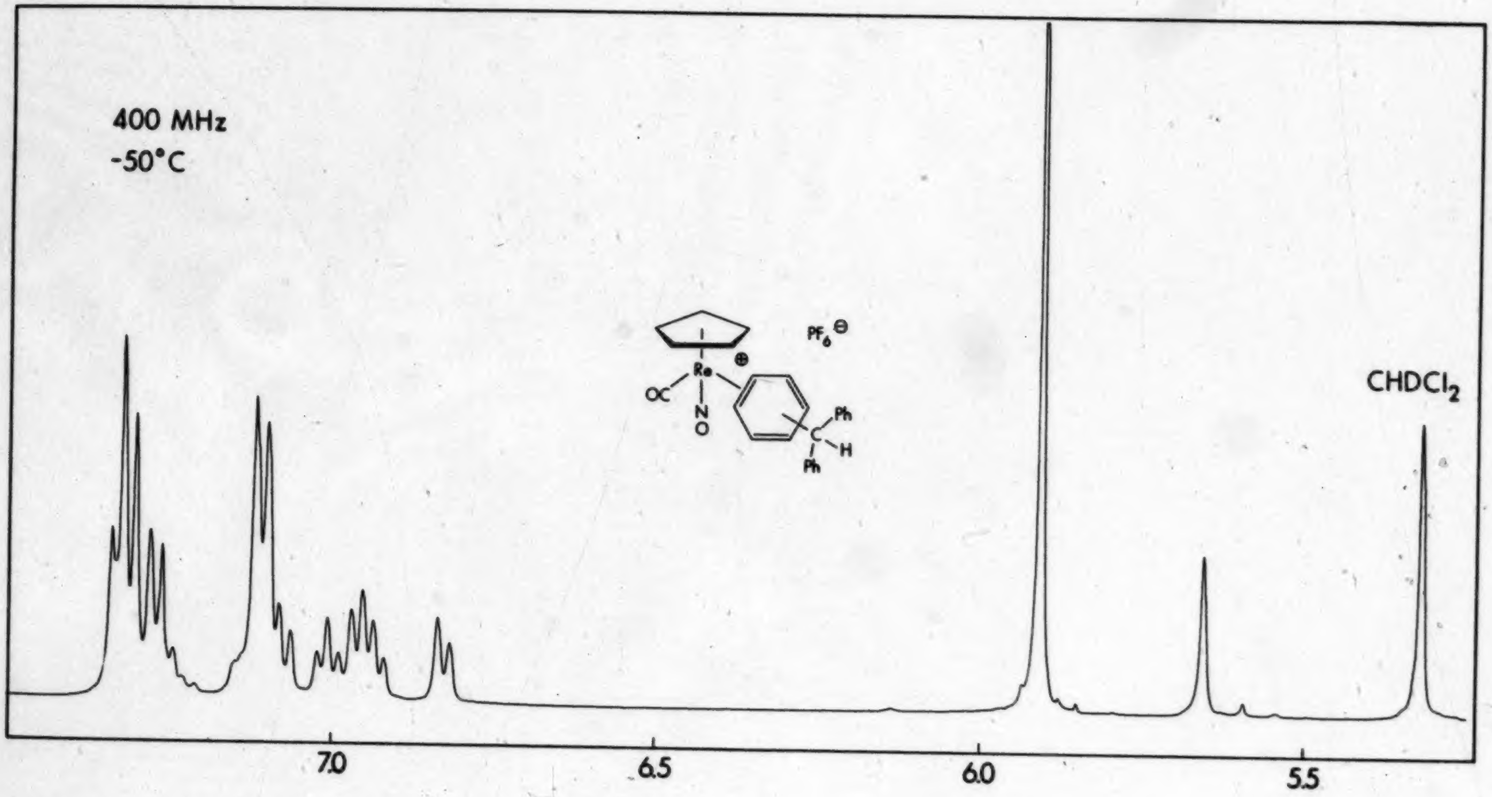
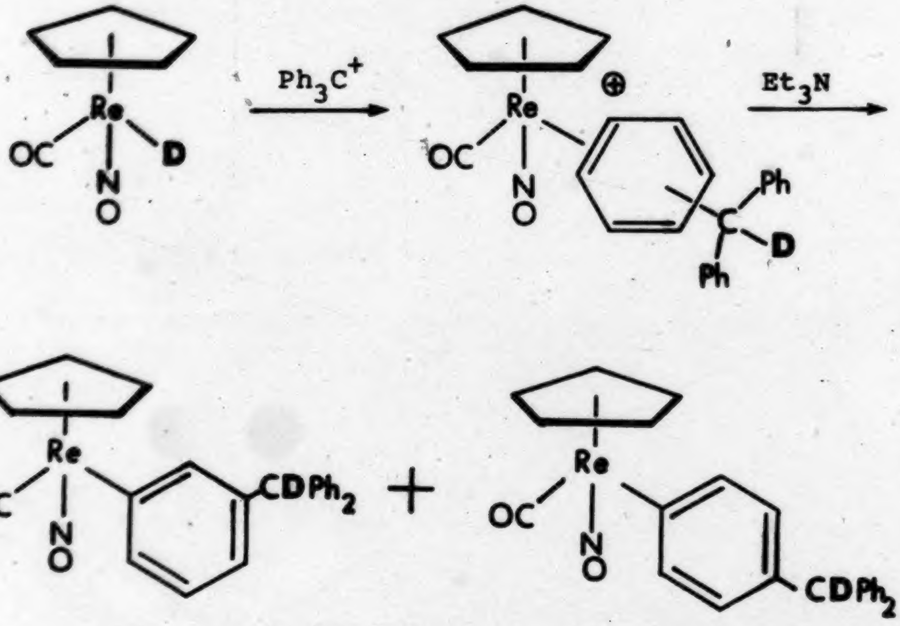


FIGURE III. ^{1}H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$, 400 MHz, CD_2Cl_2, -60°C.

out the hydridoalkyl form 13a. A transition metal hydride would be expected to resonate at much higher field, typically -10 to -20 ppm. The singlet at 5.65δ (1H) is much more consistent with the aliphatic-CPh_2H proton of the π-arene structure 13b. At higher amplitude, this singlet exhibits satellites attributed to coupling to the adjacent aliphatic carbon. The value of this coupling constant ($J(^{13}C{-}H) = 128$ Hz) is of the correct magnitude for a C_{sp^3}-H interaction.

The -CPh_2H proton at 5.65δ in 13 has been shifted to *lower field* only slightly from its position (5.56δ) in free triphenylmethane. In the aromatic region, again consistent with the π-arene structure, several small multiplets appear shifted upfield from the phenyl multiplets. These peaks are assigned to the unique phenyl ring which is coordinated to the metal center. Close proximity to rhenium would be expected to shift the resonances of these protons to higher fields.

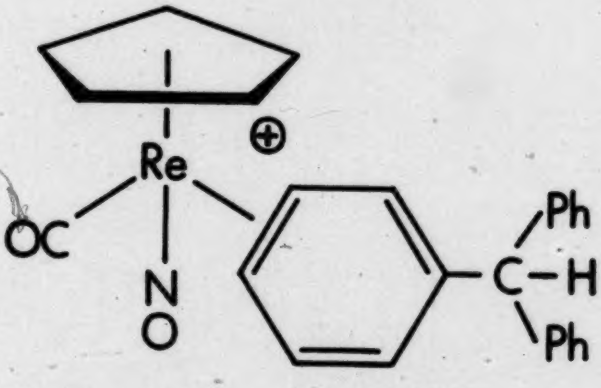
Further evidence for the structure of the triphenylmethane cation 13 comes from studies with the rhenium deuteride, $(\eta{-}C_5H_5)Re(CO)(NO)D$ (6). Reaction of this complex with trityl cation gives a triphenylmethane cation with a ^1H NMR identical to that shown in Figure III except for the singlet at 5.65δ, which is absent. Deprotonation of the triphenylmethane cation containing deuterium in the aliphatic position gave *para-* and *meta-* $(\eta\text{-}C_5H_5)(OC)(ON)ReC_6H_4CPh_2D$ [Eq (48)].



(48)

These results show that reaction of the rhenium deuteride occurs to give Ph_3CD, which then coordinates to the unsaturated $CpRe(CO)(NO)^+$ to give deuterated triphenylmethane cation. The reaction of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CD)]PF_6$ with Et_3N [Eq (48)] confirms that the protons removed were originally attached to aromatic sp^2 carbons. Deprotonation with the weak base, Et_3N, demonstrates the remarkable degree to which coordination of the rhenium group has activated one of the phenyl rings of triphenylmethane.

All the evidence discussed thus far for the structure of the triphenylmethane cation $\underset{\sim}{13}$ points to coordination of the rhenium group to one phenyl ring. The electronic requirements of the rhenium group dictate coordination to one double bond to give an 18-electron, η^2-complex. The products obtained from deprotonation with Et_3N suggest the rhenium is coordinated to the 3,4-double bond. Based on these observations the structure shown as 13c is suggested for the cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]\text{-}PF_6$.

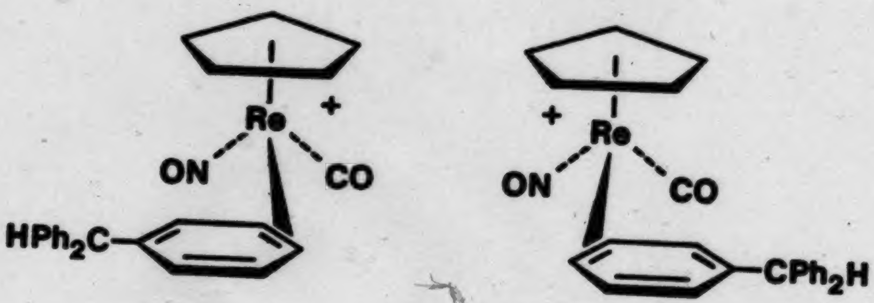


13c

As reasonable as these arguments appear, this single static structure does not totally explain the ^1H NMR of 13. As outlined in Chapter I and demonstrated in Chapter V, coordination of an unsymmetric olefin like triphenylmethane to the asymmetric rhenium group should give two diastereomers. Such diastereomers would be distinguishable by proton NMR. Diastereomers are not evident in the ^1H

NMR of the triphenylmethane cation shown in Figure III (i.e., there is only one η-C_5H_5 resonance). It may be that diastereomers in this system cannot be distinguished by proton NMR; or perhaps only one diastereomer is formed, but this seems unlikely. A more reasonable explanation for the proton NMR of 13 is interconversion of the two diastereomers shown in Scheme 11 by a process which is rapid on the NMR time scale. The observed ^1H NMR of 13 would thus represent the average environments for the protons in these two chemically distinct structures.

Scheme 11: Diastereomers of $[(\eta-C_5H_5)Re(CO)(NO)(3,4-\eta^2-C_6H_5CPh_2H)]PF_6$. Only one enantiomer is shown for each diastereomer.



Interconversion of diastereomers in the triphenylmethane cation could occur by direct migration of the rhenium group to the adjacent double bond. This would generate a ^{1}H NMR consistent with the observed results. However, if the two diastereomers of Scheme 11 represent the only structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ ($\underset{\sim}{13}$) it must be postulated that the reaction with Et_3N involves direct deprotonation of an aromatic C-H bond. Although coordination of the positive rhenium group to the 3,4 double bond might enhance the acidity of these positions, it is questionable if this would sufficiently activate the carbon-hydrogen bonds to allow facile deprotonation with Et_3N. Before addressing the question of how deprotonation of the triphenylmethane cation occurs it is of interest to examine the reported chemistry of other η^2-arene complexes.

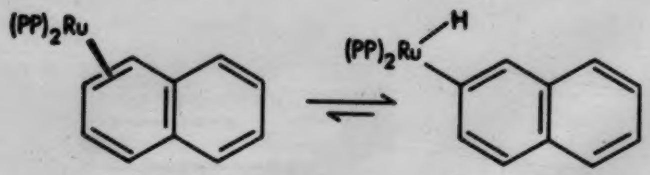
E. η^2-Arene Complexes with Transition Metals.

A large number of π-arene complexes of transition metals have been reported.[89] However, the vast majority of such compounds have structures in which the metal is bonded to the entire π-system (e.g. $(\eta^6\text{-}C_6H_6)Cr(CO)_3$). Only a few transition metal η^2-arene complexes are known and these examples contain polyfluorinated aromatic rings.

In 1973, Stone *et al.* prepared the highly fluxional molecule bis(triethylphosphine)[(hexakis(trifluoromethyl)-benzene]platinum.[90] A similar platinum phosphine complex containing perfluoro-1,2-3,4-5,6-triethanobenzene was reported by Einstein[91] in 1978. Crystal structures have been obtained for these complexes and in each case the metal was shown to be bonded to only two carbons of the aromatic ring. Dihapto coordination of the metal results in loss of aromaticity of the carbon ring. This is evidenced by non-planarity of the benzene ligand and the alternating short and long C-C distances (i.e., localized double and single bonds). In contrast to the solid state structure, where the metal interacts with only two carbons, in solution the complex is fluxional *via* metal migration about the π system.

In spite of a scarcity of isolable examples, η^2-arene complexes are commonly invoked intermediates in processes which involve activation of aromatic C-H bonds such as ortho metallation[92] and H-D exchange in arenes.[93] The beginnings of this fruitful area of study may be traced to the early work of Chatt and Davidson.[94] In 1965, these authors reported an unusual series of compounds obtained from reaction of the reduction product of $RuCl_2(dmpe)_2$ (dmpe = Me_2PCH_2-CH_2-PMe_2) with benzene, naphthalene, and other aromatic hydrocarbons. The products obtained in these reactions were shown to be $(dmpe)_2Ru(arene)$ species. However, there was some question as to the structures of the new compounds. The spectroscopic data suggested they contained hydridoaryl ligands but the chemical properties were reported to be more consistent with π-arene structures.

An X-ray study of the ruthenium compound was later reported by Gregory and co-workers[95] who also prepared the osmium analogs. It was found that in the solid state $(dmpe)_2Ru$(naphthalene) exists as a hydridonaphthyl complex. In solution this structure is in equilibrium with an η^2-naphthalene species [Eq (49)]. This tautomerism between π- and σ- complexes accounts for the chemical properties of the Ru complex such as formation of $(dmpe)_2Ru$ and naphthalene on pyrolysis.



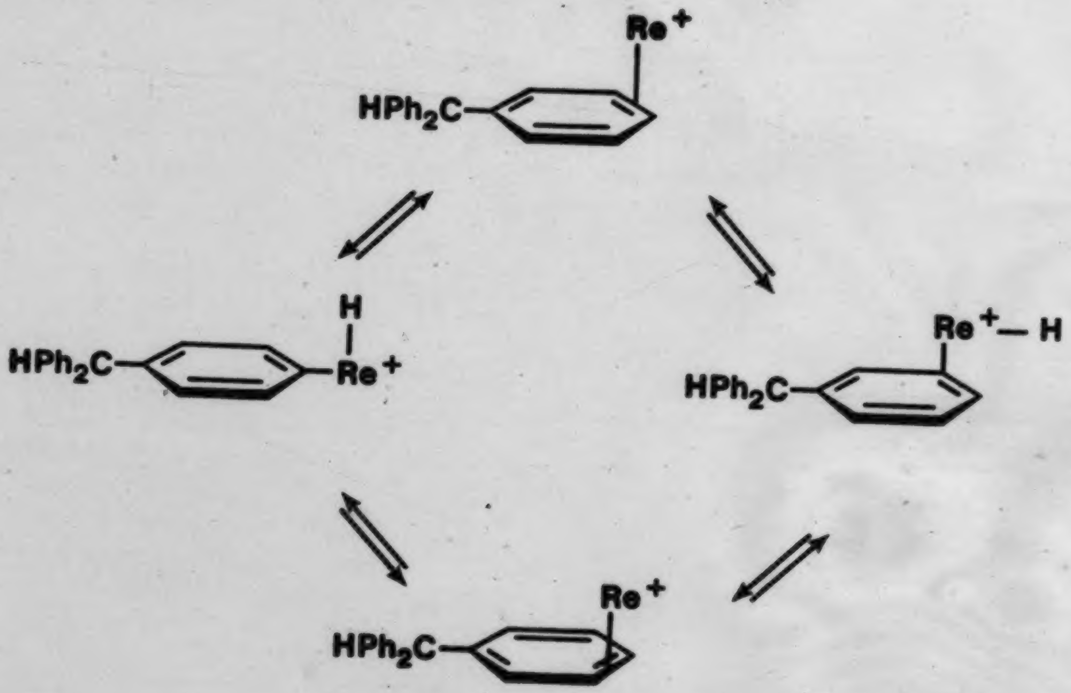
(49)

A process such as this involving prior coordination, followed by oxidative addition of the C_{aryl}-H bond to the metal is believed to be the path by which transition metals can activate aromatic carbon-hydrogen bonds.[92a,b,96] However, it appears there is, as yet, no direct experimental evidence for such a mechanism.[97]

F. The Solution Structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$

Initially a tautomerism between η^2-arene and hydridoaryl structures seemed to provide a reasonable rationale for the ^1H NMR characteristics of $(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13) and its facile deprotonation with Et_3N. The process shown in Scheme 12 would

Scheme 12: Re = $(\eta\text{-}C_5H_5)Re(CO)(NO)$-.



interconvert the diastereomers obtained on η^2-coordination of triphenylmethane to the rhenium group and provide a mechanism for activation of the ortho and para C-H bonds. In the presence of Et_3N, the hydridoaryl species would readily deprotonate to give the products obtained in Eq (46). However, a close examination of the NMR results provides strong evidence against the hydridoaryl structures of Scheme 12.

The ^1H NMR of the triphenylmethane cation (Figure III) has three small multiplets at 6.83δ (d, 1H), 6.95δ (m, 2H), and 7.01δ (t, 1H). Decoupling experiments show these signals are due to protons attached to the same phenyl ring and that the multiplet at 6.95δ is due to two different hydrogens. The observation of at least four separate signals for the phenyl ring bonded to the metal center suggests the process which interconverts the diastereomers of Scheme 11, does not equilibrate the two sides of this C_6H_5- group.* The interconversion of diastereomers *via* a para-hydridoaryl complex (Scheme 12) in which there is free rotation about the Re-C_{aryl} bond would average these phenyl protons. Thus, rapid equilibration of the structures shown in Scheme 12 would not give a ^1H NMR consistent with that of the triphenylmethane cation **13**.

An intermediate which will equilibrate the diastereomers and leave the protons of the rhenium bonded phenyl ring distinct is the σ-complex **13d**. Such a species would

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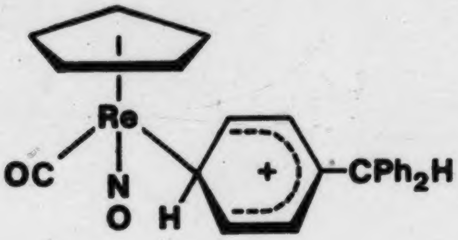
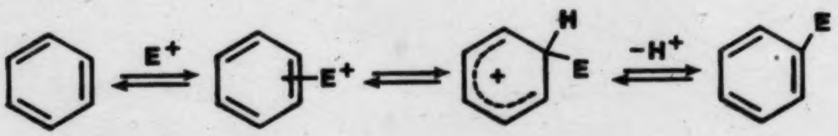
*This result also rules out interconversion of diastereomers by reversible dissociation of the triphenylmethane ligand.



13d

be formed from the 3,4-η^2 structure by electrophilic attack of the metal in the phenyl ring with formation of a sigma bond to carbon.

The sigma complex of 13d is similar to the benzonium ion intermediate of aromatic electrophilic substitution in organic chemistry. The mechanism for electrophilic substitution has been postulated[98] to involve initial formation of a π complex as shown in Eq (50). Rearrangement

 (50)

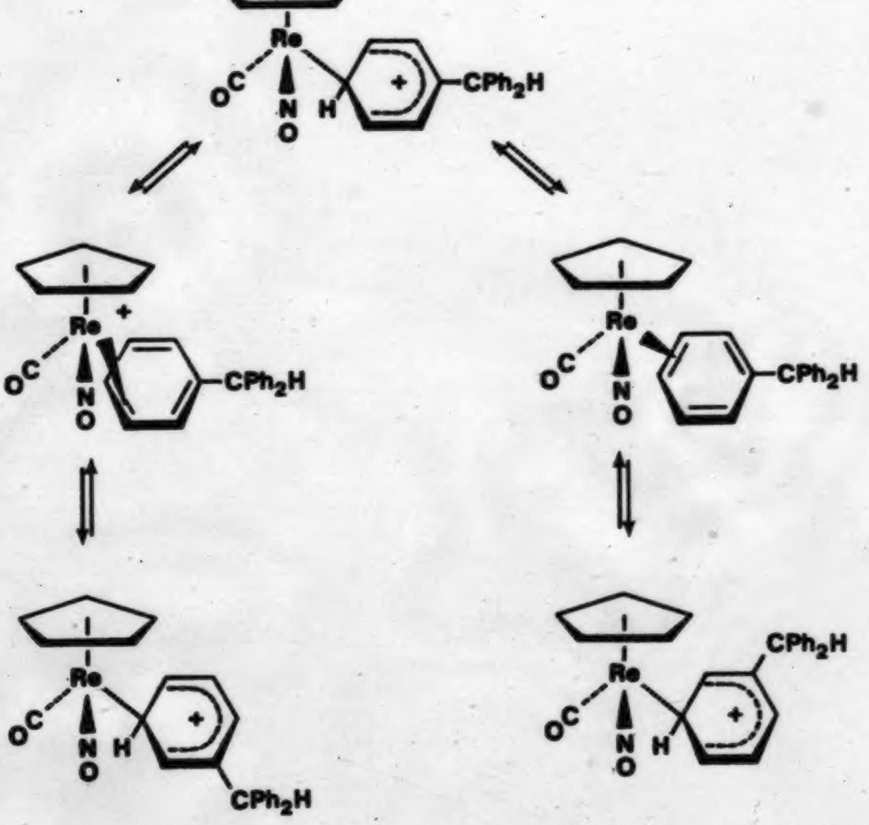
of this π intermediate gives a σ-complex from which the product is formed by deprotonation. Electrophilic substitution provides a model for the deprotonation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ with Et_3N.

Utilizing such an intermediate for interconversion of diastereomers, and remembering that both para (15) and meta (16) isomers were obtained on reaction with Et_3N, the mechanism shown in Scheme 13 is suggested to explain the ^1H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13). In each structure the two sides of the metal bonded C_6H_5 ring are non-equivalent. Thus, the weighted average should show five distinct proton signals shifted upfield from the free phenyl region. Rapid exchange of the η^2 and σ-structures of Scheme 13 would give an average ^1H NMR spectrum for the triphenylmethane cation 13 consistent with the one shown in Figure III.

It is difficult to predict the exact appearance of such an averaged NMR spectrum. Intuitively the spectrum of 13 resembles more closely that expected for the 3,4-η^2 diastereomers alone. The sigma structures would likely shift the hydrogens of the metal bonded phenyl ring and perhaps the aliphatic-CPh_2H proton from their positions in uncoordinated Ph_3CH. The overall similarity of the ^1H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ to that of uncoordinated triphenylmethane may suggest the dominance of 3,4-η^2 bonded structures.

Formation of the sigma complexes of Scheme 13, provides a path for activation of the para and meta C-H bonds of Ph_3CH. Deprotonation of the triphenylmethane

Scheme 13: Proposed Solution Structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]^+$. Only one enantiomer of each structure is shown.



Re
OC
N
O
H
+
CPh₂H

cation would occur from these intermediate structures. Failure to observe an ortho product in the reaction with Et_3N may reflect the absence of sigma structures in which the rhenium group is bonded to the ortho carbons.* On steric grounds such a structure is expected to be a high energy form. The 3,4-η^2 diastereomers should form equal quantities of the para and meta σ-complexes, provided they are of comparable energies. This agrees well with the observed 55:45 ratio of para 15 and meta 16 isomers obtained on deprotonation. The ratio of products in the Et_3N reaction would also be influenced by the relative acidities of the two types of σ-complexes.

Based on the structures of Scheme 13, the triphenylmethane cation would react with strong coordinating ligands in the pi bonded forms. Displacement of the π-arene ligand with Ph_3P would give Ph_3CH and the triphenylphosphine cation 14. The more basic ligand dimethylphenylphosphine reacts with both pi and sigma structures of 13 giving displacement and deprotonation products. The Me_2PhP reaction shows a decrease in the amount of displacement *versus* deprotonation with increasing temperature. This result could be due in part to a variance of the equilibrium constants of Scheme 13 to favor sigma structures at higher temperatures.

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*Scheme 13 could also include forms where $CpRe(CO)(NO)^+$ is η^2 bonded to the 2,3 double bonds, but the experimental data does not require such structures.

* * * * *

The characteristics of the triphenylmethane cation (e.g., insolubility, low thermal stability, very complex ^{1}H NMR) present many problems in the determination of the solution structures of this unusual compound. Presumably simpler arene derivatives of this system would prove more amenable to such studies. Hopefully, the future preparation of other $[(\eta\text{-}C_5H_5)Re(CO)(NO)(arene)]^+$ complexes will provide further insight into the structures of this novel class of compounds.

SECTION IV

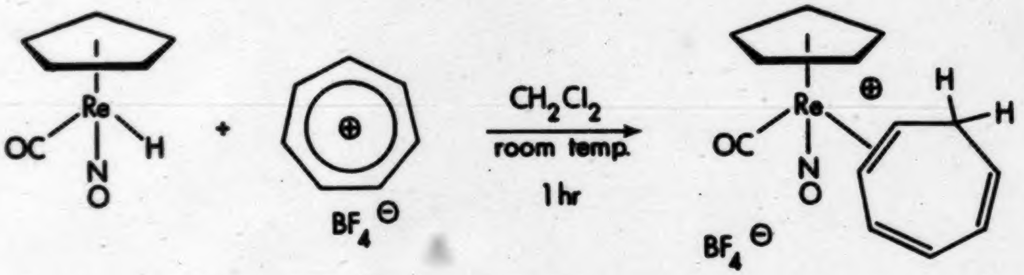
REACTIONS OF $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ WITH OTHER ELECTROPHILES

The reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with trityl cation occurs with hydride abstraction to generate triphenylmethane. The isolated product $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]\text{-}PF_6$ ($\underset{\sim}{13}$), obtained at low temperatures contains Ph_3CH coordinated through a phenyl ring to the metal center. Although the properties of the triphenylmethane cation are not consistent with the hydridoalkyl structure $\underset{\sim}{13}$a such an intermediate may initially be formed and then rearrange to the isolated product. A study of reactions of the rhenium hydride $\underset{\sim}{5}$ with other electrophiles was undertaken in an attempt to isolate such a complex. Reaction of $\underset{\sim}{5}$ with CH_3^+, for example, might be expected to form the hydridomethyl cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(H)\text{-}(CH_3)]^+$.

No reaction was observed on treatment of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with Me_3OPF_6, CH_3OSO_3F, or Et_3OBF_4. Attempts to protonate $\underset{\sim}{5}$ with the strong acid $HBF_4\text{-}Et_2O$ are still in a preliminary stage. The hydride does react with this acid but the results of protonation will have to await further study.

The only electrophile other than trityl cation which has been found to abstract H^- from the hydride is tropylium tetrafluoroborate. Reaction of the rhenium hydride 5 with $C_7H_7^+$ occurs rapidly in CH_2Cl_2 at room temperature to give $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) [Eq (51)]. In contrast to the η^2-arene complex the

(51)



η^2-olefin compound 18 shows excellent thermal and oxidative stability. There is no evidence for nonrigidity or ligand displacement in the chemistry* of the η^2-cycloheptatriene complex.

It is noteworthy that the reaction shown in Eq (51) can also be carried out in THF. A separate experiment showed cycloheptatriene will not displace THF from the $[(\eta\text{-}C_5H_5)Re(CO)(NO)(THF)]^+$ cation. This may suggest the abstraction-coordination process of Eq (51) is concerted. The reaction of $C_7H_7^+$ with $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ was monitored at low temperature (^1H NMR) in an attempt to observe a hydrido-alkyl intermediate, $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(H)(C_7H_7)]^+$. This study showed only direct formation of

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*The characterization and chemical properties of 18 are described in Chapter V.

18. If an intermediate complex is involved in Eq (51) it must be rapidly converted to the final η^2-C_7H_8 product.

The reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with tropylium cation $(C_7H_7)^+$ is analogous to that with the trityl cation (Ph_3C^+). Isolation of 18 in which the rhenium group is coordinated to one double bond of cycloheptatriene provides further evidence for the structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ suggested in Section III.

SECTION V

FURTHER COMMENTS ON THE BEHAVIOR OF $(\eta\text{-}C_5H_5)Re(CO)(NO)H$.

The initial report[12] on the preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) suggested this compound was very unusual for a carbonyl-η-cyclopentadienyl transition metal hydride. The lack of reactivity encountered in the present investigation of the chemistry of 5 seemed to confirm the suspicion. Further studies were undertaken on the only mode of reaction exhibited by $(\eta\text{-}C_5H_5)Re(CO)(NO)H$; reaction with electrophiles. Although 5 showed similar behavior to the Group VIb tricarbonyls on treatment with trityl cation (i.e., H^- abstraction) the isolated products were very much different. Once again the rhenium hydride appeared to show anomolous properties.

As $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) is also a *nitrosyl*-η-cyclopentadienyl hydride, perhaps the NO ligand greatly influences its behavior. This suggestion was strengthened by the work of Legzdins[99] on $(\eta\text{-}C_5H_5)W(NO)_2H$ reported in 1979. Like 5, this nitrosyl hydride shows no proton donor properties. The chemistry of the bis-nitrosyl complex is dominated by its tendency to function as a source of H^-. However, the thermal and oxidative stability of the tungsten hydride is much less than that exhibited by $(\eta\text{-}C_5H_5)Re(CO)(NO)H$. Furthermore, the similarity in the electronic and steric properties of CO and NO suggest the presence of a nitrosyl ligand would not greatly change the properties of $\underset{\sim}{5}$ from that of other carbonyl hydrides.

The most direct comparison to $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ would be the corresponding Mn and Tc hydrides. Unfortunately neither of these compounds has been isolated. All attempts[13,14,100] to prepare the manganese complex have given the dimer $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$, presumably *via* the unstable hydride. In 1980, Legzdins[100] obtained further evidence for the instability of $(\eta\text{-}C_5H_5)Mn(CO)(NO)H$. The triphenylphosphine derivative of this hydride was prepared and found to have very low air and thermal stability. The properties of the manganese hydrides suggested the metal as the source of stability in $(\eta\text{-}C_5H_5)Re(CO)(NO)H$. The influence of a third row transition metal is evident from a comparison of the stabilities of the Group VIb tricarbonyl hydrides (Section I-B).

Even more enlightening is the current investigation by Hoyano and Graham[101] of the little known $(\eta\text{-}C_5H_5)Os(CO)_2H$. The osmium hydride shows excellent air and thermal stability; comparable to that of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$. In contrast to the Fe and Ru analogs, $(\eta\text{-}C_5H_5)Os(CO)_2H$ is resistant to deprotonation. No evidence has yet been obtained for the anion, $CpOs(CO)_2^-$. Reaction of the osmium hydride with the electrophiles Ph_3C^+ and $C_7H_7^+$ gave $\eta^2\text{-}Ph_3CH$ and

η^2-C_7H_8 cations similar to those of the rhenium hydride $\underset{\sim}{5}$. The lack of obvious H^+ and H^- donor properties for the osmium and rhenium hydrides may largely be due to the strength of the metal-hydrogen bonds.

With the knowledge of these recent results the behavior of $(\eta$-$C_5H_5)Re(CO)(NO)H$ no longer seems entirely unique. Work is currently underway in this research group to extend the reactions of the rhenium hydride to other metal systems. Initial results obtained with iron group dicarbonyl hydrides show reactions modes somewhat similar to those of $\underset{\sim}{5}$. It seems probable that many of the processes first observed with $(\eta$-$C_5H_5)Re(CO)(NO)H$ will prove to be general reactions of transition metal hydrides.

SECTION VI

EXPERIMENTAL

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$:

$(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.5 g, 1.61 mmol) was dissolved in 25 mL of acetone and cooled to 0°C. Bromine (0.098 mL, 1.90 mmole) was added dropwise and the solution refluxed for 2 hrs at 60°C. The solvent was removed under reduced pressure to give a dark red solid. This material was placed on a Florisil (100-200 mesh) column and eluted with benzene. A red band moved quickly down the column, was collected, and the solvent removed to give the bromide as red microcrystals, 0.52 g, 83% yield, M.P. 133-134°C.

Characterization: IR (hexane) 2003(s), $\nu(CO)$; 1742(s) cm^{-1}, $\nu(NO)$. Mass Spectrum, 90°C/16 ev: $[CpRe(CO)(NO)Br]^+$, $[CpRe(NO)Br]^+$, $[CpReBr]^+$. Proton NMR (CD_2Cl_2) δ 5.86 ppm. Anal. Calcd for $C_6H_5ReO_2NBr$: C, 18.51; H, 1.29; N, 3.60. Found: C, 18.51; H, 1.29; N, 3.57.

Reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ with CBr_4:

Carbon tetrabromide (0.22 g, 0.64 mmole) and $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ were heated in 10 mL of benzene at 60°C for 2 hrs. The solvent was removed under reduced pressure to give a black solid. This material was placed on a florisil (100-200 mesh) column and eluted with benzene. A red band quickly moved down the column, was collected, and the solvent removed under reduced pressure to give red, microcrystals of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$, 0.13 g, 52% yield.

The compound was identified by comparison of its infrared, proton NMR and mass spectra with authentic samples.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(CH_3CN)PF_6$:

$(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.5 g, 1.61 mmol) was dissolved in 20 mL of acetonitrile and cooled to 0°C. Triphenylcarbenium hexafluorophosphate (0.625 g, 1.61 mmol) dissolved in 10 mL of CH_3CN was added dropwise to give a bright yellow solution. The addition of diethylether gave a precipitate which was collected and washed with 3 x 20 mL of ether to give the acetonitrile cation as yellow, microcrystals, 0.75 g, 94% yield.

Characterization: IR (CH_2Cl_2) 2030(s), ν(CO); 1769(s) cm^{-1}, ν(NO). Proton NMR δ 6.08 (5H), 2.82 (3H) ppm. Anal. calcd for $C_8H_8ReO_2N_2PF_6$: C, 19.40; H, 1.63; N, 5.65. Found: C, 19.47; H, 1.63; N, 5.56.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_4H_8O)PF_6$:

$(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.1 g, 0.32 mmol) was dissolved in 5 mL of THF and cooled to 0°C. Triphenylcarbenium hexafluorophosphate (0.125 g, 0.32 mmol) in 5 mL of CH_2Cl_2 was added dropwise. The solution became yellow and a yellow precipitate appeared. The addition of diethylether gave more of the precipitate, which was collected and washed with 3 x 10 mL of ether to give yellow microcrystals of the THF cation, 0.077 g, 45% yield.

Characterization: IR (CH_2Cl_2) 2017(s), ν(CO); 1755(s) cm^{-1}, ν(NO). Proton NMR (CD_2Cl_2) δ 6.12 (5H), 4.24 (m, 4H), 2.12 (m, 4H) ppm. Anal. calcd for $C_{10}H_{13}ReO_3NPF_6$: C, 22.82; H, 2.49; N, 2.66. Found: C, 22.56; H, 2.29; N, 2.78.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_3H_6O)PF_6$:

$(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.1 g, 0.32 mmol) was dissolved in 5 mL of acetone and cooled to 0°C. Triphenylcarbenium hexafluorophosphate (0.125 g, 0.32 mmol) in 5 mL of acetone was added dropwise to give a reddish-yellow solution. The addition of diethylether gave a precipitate which was collected, and washed with 3 x 10 mL of ether to give the acetone cation as yellow, microcrystals, 0.055 g, 33% yield.

Characterization: IR (CH_2Cl_2) 2019(s), ν(CO); 1757(s) cm^{-1}, ν(NO). Proton NMR (CD_2Cl_2) δ 6.16 (5H), 2.66 (6H) ppm. Anal. Calcd for $C_9H_{11}ReO_3NPF_6$: C, 21.10; H, 2.16; N, 2.73. Found: C, 21.29; H, 2.09; N, 2.89.

Preparation of $(\eta-C_5H_5)Re(CO)(NO)(Ph_3CH)PF_6$:

Triphenylcarbenium hexafluorophosphate (0.125 g, 0.32 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to -78°C. $(\eta-C_5H_5)Re(CO)(NO)H$ (0.10 g, 0.32 mmol) was added as a solid in four equal portions over ~15 min. The solution turned reddish-yellow and within 0.5 hrs a yellow precipitate appeared. The solution was filtered at -78°C, and the solid washed with 2 x 5 mL of cold CH_2Cl_2 to give yellow microcrystals of the triphenylmethane cation, 0.21 g, 93% yield.

Characterization: IR (CH_2Cl_2) 2026(br,s), ν(CO); 1765 (br,s) cm^{-1}, ν(NO). Proton NMR (see discussion). Anal. calcd for $C_{25}H_{21}ReO_2NPF_6$: C, 42.98; H, 3.12; N, 2.00. Found: C, 42.96; H, 3.02; N, 2.11.

Reactions of $(\eta-C_5H_5)Re(CO)(NO)(Ph_3CH)PF_6$

(a) With triphenylphosphine -

Preparation of $(\eta-C_5H_5)Re(CO)(NO)(PPh_3)PF_6$:

Triphenylcarbenium hexafluorophosphate (0.125 g, 0.32 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to -78°C. $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.10 g, 0.32 mmol) was added as a solid in four equal portions over ~15 min to give a reddish-yellow solution. Triphenylphosphine (0.085 g, 0.32 mmol) was added and the resulting yellow solution stirred at -78°C for 1 hr then warmed to room temperature. The addition of diethylether gave a precipitate which was collected, and washed with 3 x 10 mL of ether to give the triphenylphosphine cation as yellow microcrystals, 0.22 g, 96% yield.

Characterization: IR (CH_2Cl_2) 2023(s), ν(CO); 1767(s) cm^{-1}, ν(NO). Proton NMR δ 5.83 (5H), 7.5 (m, 15H) ppm. Anal. Calcd for $C_{24}H_{20}ReO_2NP_2F_6$: C, 40.23; H, 2.81; N, 1.95. Found: C, 40.49; H, 2.80; N, 1.92.

Reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)PF_6$:

(b) With Triethylamine -

Preparation of *para* and *meta* $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_6H_4CPh_2)H$:

Triphenylcarbenium hexafluorophosphate (0.625 g, 1.61 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to -78°C. $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.50 g, 1.61 mmol) was added as a solid in four equal portions over ~15 min to give a reddish-yellow solution. Triethylamine (0.90 mL, 6.47 mmol) was added and the resulting red solution stirred at -78°C for 1 hr. After warming to room temperature, the solvent was removed under reduced pressure to give a red solid. This solid was extracted with hexane, the extracts filtered and cooled to -78°C to give pink crystals of *para* and *meta* $(\eta\text{-}C_5H_5)Re(CO)(NO)C_6H_4CPh_2H$ 0.79 g, 89% yield. The *para* and *meta* isomers occur in a 55:45 mixture which may be separated by repeated fractional recrystallization from CH_2Cl_2/hexane.

Characterization: *para* isomer: IR (hexane) 1982.4(s), ν(CO); 1731.3(s) cm^{-1}, ν(NO). Mass Spectrum, 120°C/24 ev: $[CpRe(CO)(NO)C_6H_4CPh_2H]^+$, $[CpRe(NO)C_6H_4CPh_2H]^+$, $[CpReC_6H_4CPh_2H]^+$. Proton NMR (see discussion). Anal. Calcd for $C_{25}H_{20}ReO_2N$: C, 54.33; H, 3.65; N, 2.53. Found: C, 54.04; H, 3.65; N, 2.57.

meta isomer: IR (hexane) 1981.6(s), ν(CO); 1730.7(s) cm^{-1}, ν(NO). Mass Spectrum, 120°C/20 ev: $[CpRe(CO)(NO)C_6H_4CPh_2H]^+$, $[CpRe(NO)C_6H_4CPh_2H]^+$, $[CpReC_6H_4CPh_2H]^+$. Proton NMR (see discussion). Anal. Calcd for $C_{25}H_{20}ReO_2N$: C, 54.33; H, 3.65; N, 2.53. Found: C, 54.09; H, 3.64; N, 2.59.

(c) With Dimethylphenylphosphine -

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(PMe_2Ph)PF_6$:

Triphenylcarbenium hexafluorophosphate (0.625 g, 1.61 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to -78°C. $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (0.50 g, 1.61 mmol) was added as a solid in four equal portions over ~15 min to give a reddish-yellow solution. Dimethylphenylphosphine (0.25 mL, 1.69 mmol) was added and the resulting orange solution stirred for 1 hr at -78°C then warmed to room temperature. The addition of diethylether gave a precipitate which was collected and washed with 3 x 20 mL of ether to give the dimethylphenylphosphine cation as yellow microcrystals, 0.55 g, 58% yield (see discussion).

Characterization: IR (CH_2Cl_2) 2022(s), ν(CO); 1771(s) cm^{-1}, ν(NO). Proton NMR (CD_2Cl_2) δ 5.83 (5H), 7.68 (m, 5H), 2.285 (d, 3H), 2.291 (d, 3H) ppm; $J(CH_{3a}-P) \simeq J(CH_{3b}-P) = 10.7$ Hz. Anal. Calcd for $C_{14}H_{16}ReO_2NP_2F_6$: C, 28.38; H, 2.72; N, 2.36. Found: C, 28.34; H, 2.69; N, 2.43.

Protonation of *para* and *meta* $(\eta-C_5H_5)Re(CO)(NO)(C_6H_4CPh_2H)$:

An equimolar mixture of *para* and *meta* $(\eta-C_5H_5)Re(CO)(NO)(C_6H_4CPh_2H)$ (0.10 g, 0.18 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to -78°C. The addition of HBF_4/Et_2O gave a yellow-orange solution from which slowly precipitated a yellow solid. The solid was collected by filtration at -78°C, and washed with 2 x 5 mL of cold CH_2Cl_2. Infrared and proton NMR spectroscopy showed this material to be the triphenylmethane cation, $(\eta-C_5H_5)Re(CO)(NO)(CPh_3H)BF_4$, 0.116 g, 82% yield.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)BF_4$:

Tropilium tetrafluoroborate (0.057 g, 0.32 mmol) and $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ were stirred in 5 mL of CH_2Cl_2 for 1 hr at room temperature. The addition of diethylether to this yellow solution gave a precipitate, which was collected, and washed with 3 x 10 mL of ether to give yellow microcrystals of the cycloheptatriene cation, 0.146 g, 93% yield.

Characterization: IR (CH_2Cl_2) 2057(br,s) ν(CO); 1778(br,s) cm^{-1}, ν(NO). Proton NMR (see discussion). Anal. Calcd for $C_{13}H_{13}ReO_2NBF_4$: C, 31.98; H, 2.68; N, 2.87. Found: C, 31.78; H, 2.62; N, 2.83.

CHAPTER IV

DINUCLEAR PRODUCTS OF THE RHENIUM GROUP

SECTION I

INTRODUCTION

The previous chapter described a series of compounds obtained in a study of hydride abstraction from $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5). The reaction of trityl cation with 5 can be used to prepare cations of the type, $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$, which are themselves valuable synthetic intermediates. In the present chapter similar reactions are explored which provide convenient routes to dinuclear derivatives of the rhenium group.

A. Carbonyl-η-Cyclopentadienyl Metal Dimers.

A number of transition metal carbonyls are known which contain two or more metal centers. The compounds range from the simple dinuclear carbonyls (e.g. $Re_2(CO)_{10}$) to polynuclear complexes such as $Rh_6(CO)_{16}$. Studies of polynuclear metal carbonyls have traditionally focused on the many structural and bonding modes exhibited by these types of complexes.* Beginning in 1973, when Kaesz[103] first drew attention to the analogy of cluster chemistry to reactions on metal surfaces, this area of organometallic chemistry has greatly expanded. Much of current research on metal carbonyl clusters emphasizes their use as homogeneous catalysts and catalytic models.[104]

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*A number of reviews have been published on transition metal clusters.[102]

In the present study, a series of compounds has been prepared, each of which contains two units of the CpRe(CO)(NO)- group. The parent molecule in this series is the rhenium dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. This compound is one of a class of dinuclear species containing carbonyl-η-cyclopentadienyl ligands and metal-metal bonds. Among the best known examples are the chromium group tricarbonyl $[(\eta\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr,[76] Mo, W[105]) and the dicarbonyl dimers of the iron triad, $[(\eta\text{-}C_5H_5)M(CO)_2]_2$ (M = Fe,[106] Ru,[107] Os[108]). These dimers show many similarities in their reactions, structures, and bonding. A molecular orbital treatment of the bonding in the iron group dimers can be found in a recent publication by Hoffmann.[109]

Many reactions of the carbonyl-η-cyclopentadienyl metal dimers occur with cleavage of the metal-metal bond to give mononuclear species. However, other reactions produce dinuclear complexes in which some metal-metal bonding remains. Protonation[86,110] of the dimers, for example, gives hydride bridged cations [Eq (52)]. These

$$[(\eta\text{-}C_5H_5)M(CO)_X]_2 \xrightarrow{H^+} [(\eta\text{-}C_5H_5)M(CO)_X](\mu_2\text{-}H^+) \quad (52)$$

X = 2; M = Fe, Ru

X = 3; M = Mo, W.

complexes probably have structures in which the hydrogen is bonded equally to both metals while a metal-metal bond is maintained. The bridged hydride cations form part of another group of polynuclear compounds called hydrido clusters. Reviews on the chemistry of hydrido clusters can be found in the general reports on metal hydrides,[60,75] and in two more specialized articles by Kaesz.[103,111]

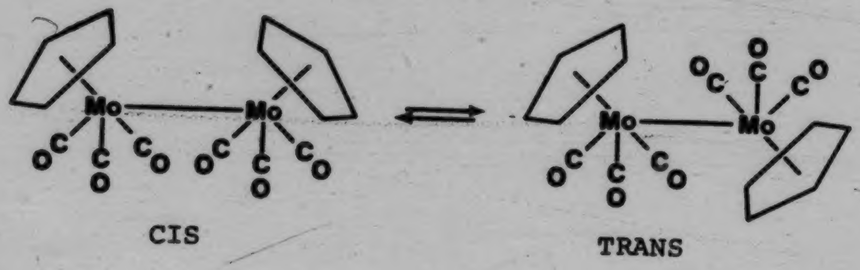
In still other reactions, the carbonyl-η-cyclopentadienyl dimers have given dinuclear products without metal-metal bonding. Controlled halogenation of the iron and ruthenium dimers[112] has been used to prepare bridged halide cations $[(\eta\text{-}C_5H_5)M(CO)_2](\mu_2\text{-}X)^+$, M = Fe, Ru; X = halogen. Application of the 18-electron rule to these compounds suggests there would be no direct bonding between the metal centers. The absence of a metal-metal bond in the iodo bridged iron dimer has been confirmed by an X-ray study.[113]

The degree of metal-metal interaction in such dinuclear complexes was for many years a hotly debated subject. The 18-electron rule and spectroscopic evidence can be used to postulate structures but the final confirmation requires X-ray or neutron diffraction studies. The results of a crystal structure analysis can also be open to various interpretations, particularly for bridged hydride complexes. For a discussion of this problem and a comparison of M-M, M-(μ_2-H)-M and M-(μ_2-Cl)-M bonds the reader is referred to recent papers by Dahl, *et al.*[114] and by Churchill.[115]

B. Stereochemical Nonrigidity in Carbonyl-η-Cyclopentadienyl Metal Dimers.

The most widely studied aspect of the chemistry of carbonyl-η-cyclopentadienyl metal dimers has been the variety of structures they exhibit in solution and the interconversion of these structures. All six chromium and iron group dimers show stereochemical nonrigidity detectable by infrared and NMR spectroscopy. In solution these compounds exist as a rapidly exchanging mixture of two or more structural forms. A review has been published discussing nonrigidity in metal carbonyl dimers and the methods used to study such processes.[116]

The Mo dimer $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$, has pentahapto-cyclopentadienyl groups and six terminal carbonyl ligands. Utilizing the 18-electron rule there are two possible structures for this complex. As shown in Eq (53) the molecule could have a cis or trans arrangement with respect to the cyclopentadienyl ligands. In the solid state, $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ has the trans structure.[117] A 1972 study by Adams and Cotton[118] found that in solution this complex exists as a rapidly exchanging mixture of the cis

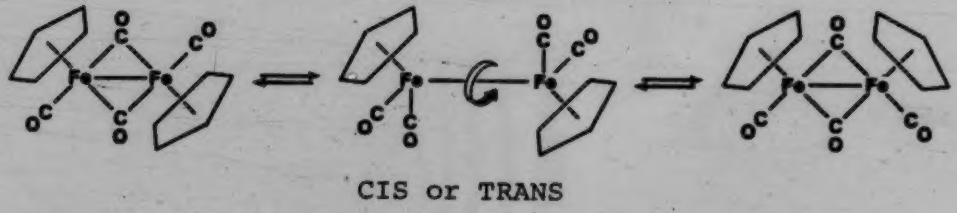


(53)

and trans forms. At −15°C, the ^{1}H NMR showed two cyclopentadienyl signals separated by *ca.* 0.2 ppm. These peaks were assigned to cis and trans isomers. The signal at higher field was more abundant in polar solvents and was thus attributed to the cis conformation. On warming the signals broadened and coalesced to give one sharp peak at +62°C. At this temperature the exchange of cis and trans isomers is rapid on the NMR time scale, giving one averaged signal for both structures. The interconversion of cis and trans forms is believed to occur intramolecularly, by rotation about the Mo-Mo bond. The two geometric isomers can also be distinguished by infrared spectroscopy. Analogous behavior has been reported for the Cr and W dimers.[119]

The iron dimer $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ shows similar nonrigidity but the process is more complex due to the presence of bridged carbonyl ligands. The bridging forms of the iron dimer contain pentahaptocyclopentadienyl groups with two terminal and two bridging CO ligands. In the solid state,[120] the compound has trans or cis structures depending on the polarity of the solvent used for crystallization. In solution, $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ exists as an equilibrium among cis and trans, bridged and nonbridged forms (Scheme 14). Rapid exchange of these structures occurs by bridge-terminal exchange of CO ligands and by internal rotation about the Fe-Fe bond in the nonbridged forms. These processes have been delineated by the use of proton and carbon NMR correlated with infrared data.[121] Similar behavior may occur in $[(\eta\text{-}C_5H_5)Ru(CO)_2]_2$[122] but with a much higher concentration of cis and trans nonbridged structures. The osmium dimer exhibits only

Scheme 14:



cis and trans unbridged structures.[101] These results suggest the tendency of carbon monoxide to bridge metal-metal bonds decreases on descending a group of the periodic table.

Bridge-terminal exchange is not unique to carbonyl ligands. Studies on the nitrosyl dimers, $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ and $[(\eta\text{-}C_5H_5)Cr(NO)_2]_2$, were reported in 1973 by Ibers, Marks, *et al.*[123] The infrared and ^1H NMR data for these compounds showed bridge-terminal exchange also occurs with nitrosyl ligands and at a rate comparable to the carbonyl process. The nonrigid behavior of $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ will be more fully discussed in Section IV-C.

The above studies suggest a relatively small energy difference between structures having bridged and terminal CO/NO ligands, and also between cis and trans isomers. Small changes in environment or the nature of the complex can greatly alter the structure of such dinuclear compounds. The stereochemical nonrigidity of other η-cyclopentadienyl metal dimers suggested similar behavior might be possible for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$.

SECTION II

CHEMISTRY OF $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$.

The previous chapter outlined some reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$) with electrophiles. Alkyl cations like Ph_3C^+ abstract H^- from the hydride, giving formally, coordinately unsaturated $CpRe(CO)(NO)^+$ which undergoes further reactions. A similar process occurs when the rhenium bromide $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ ($\underset{\sim}{9}$)* is reacted with trimethyloxonium hexafluorophosphate (Me_3OPF_6).

A. Preparation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$.

When a red solution of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ ($\underset{\sim}{9}$) was treated with Me_3OPF_6 in CH_2Cl_2 a slow reaction occurred over a period of *ca.* 8 hr to give a reddish-orange color. Infrared monitoring indicated formation of a cationic compound of the rhenium group. Proton NMR of the product mixture showed MeBr and cyclopentadienyl signals in the region expected for rhenium cations. Addition of diethylether gave orange, air stable, microcrystals. Elemental analysis of the new compound was consistent with its formulation as the brominated dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2\text{-}(Br)PF_6$ ($\underset{\sim}{19}$) [Eq (54)].

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*The preparation and characterization of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ have been discussed in Chapter III.

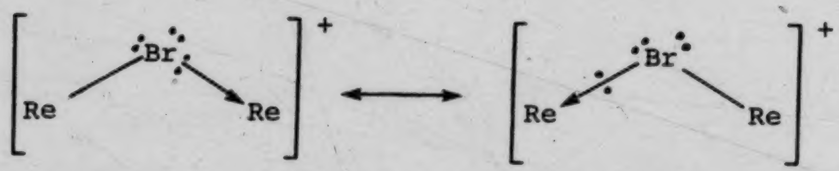
$$2(\eta\text{-}C_5H_5)Re(CO)(NO)Br + 1Me_3OPF_6 \longrightarrow [(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(Br)PF_6 + MeBr + Me_2O \qquad (54)$$

The nature of the rhenium product, and the presence of MeBr suggests the initial step of Eq (54) involves Br^- abstraction from (19). This process may occur by direct attack of CH_3^+ at bromine. Alternatively electrophilic attack at the metal center would give $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Br)CH_3]^+$ which could reductively eliminate methyl bromide. The formal product of bromide abstraction is the electronically and coordinately unsaturated $CpRe(CO)(NO)^+$. This presumed intermediate would readily coordinate a second molecule of (9) through one of the lone pairs on bromine to give the observed dinuclear product $[(\eta\text{-}C_5H_5)Re(CO)(NO)](\mu_2\text{-}Br)^+$. The relatively low yield of (19), 38%, is likely due to the instability of Me_3OPF_6 in solution; unreacted $(\eta\text{-}C_5H_5)$-$Re(CO)(NO)Br$ was detected in the reaction mixture.

The route used to prepare (19) is very similar to those reported to give the iron analog $[(\eta\text{-}C_5H_5)Fe(CO)_2]$-$(\mu_2\text{-}Br)^+$. The iron compound was obtained on reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2Br$ with the Lewis acids, $AlBr_3$ or $BF_3 \cdot OEt_2$.[124] Similarly treatment of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ with $AgBF_4$ generates the corresponding bridged iodide complex. A thorough mechanistic study of the latter reaction has recently been carried out by Mattson and Graham.[125]

B. Reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$.

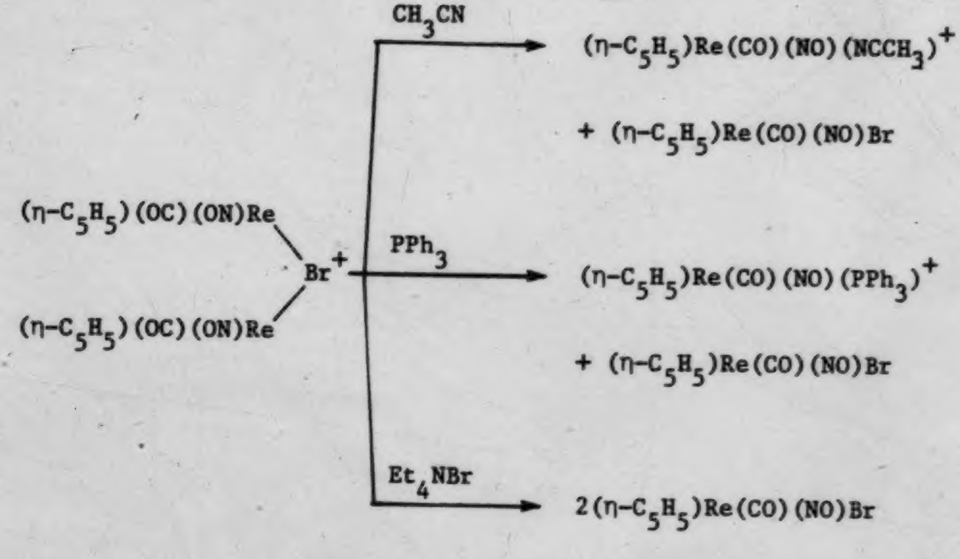
The bonding in the bridged bromide dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)^+$ can be represented by the two resonance structures shown below. In each canonical



form, the bromine atom is formally sigma bonded to one neutral rhenium fragment while donating a lone pair of electrons to the other, cationic rhenium. This complex may be considered a cation of the type $CpRe(CO)(NO)L^+$, where L is a two-electron neutral ligand; in this case CpRe(CO)(NO)Br. This view suggests the bridged bromide (19) would be susceptible to cleavage by displacement of the rhenium bromide ligand. This postulate was confirmed by the reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$ (19), summarized in Scheme 15. The products of these reactions have all been prepared separately in this study. Their presence was established by comparison of infrared and ^1H NMR spectra to authentic samples.

The chemistry of the bridged bromide (19) is dominated by displacement of the coordinated CpRe(CO)(NO)Br unit. Donor ligands (L) such as CH_3CN and PPh_3 rapidly cleave the bromide bridge to give a 1:1 mixture of

Scheme 15.


CH3CN
(η-C5H5)Re(CO)(NO)(NCCH3)+
+ (η-C5H5)Re(CO)(NO)Br
(η-C5H5)(OC)(ON)Re
Br+
(η-C5H5)(OC)(ON)Re
PPh3
(η-C5H5)Re(CO)(NO)(PPh3)+
+ (η-C5H5)Re(CO)(NO)Br
Et4NBr
2(η-C5H5)Re(CO)(NO)Br

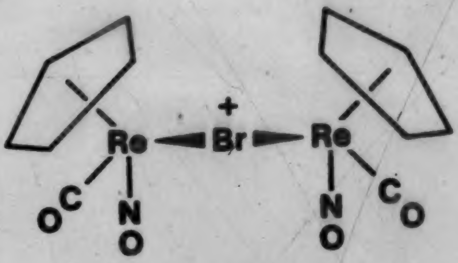
$(\eta\text{-}C_5H_5)Re(CO)(NO)L^+$ and (9). With the anionic nucleophile Br^-, an instantaneous reaction occurs to give two moles of the neutral bromide $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$. Similar reactions of the bridged halide dimers, $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2(\mu_2\text{-}Br)PF_6$ and $[(\eta\text{-}C_5H_5)Ru(CO)_2]_2(\mu_2\text{-}X)PF_6$, X = Cl, Br, I with neutral and anionic nucleophiles have been reported by Haines, *et al.*[112b] and by Fischer.[124]

C. The Structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$.

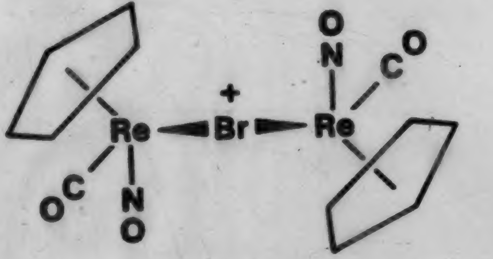
In contrast to the parent metal-metal bonded dimers little study has been devoted to the structures of the halogen bridged compounds. Infrared and NMR data have been reported for the $[(\eta\text{-}C_5H_5)M(CO)_2]_2X^+$

(M = Fe,^{124,112a,125} Ru^{112b}) complexes with little discussion as to the structures they might imply. Solid state data is available from the X-ray study of the iodo-bridged dimer, $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2(\mu_2\text{-}I)BF_4$ reported in 1973.^{113} The crystal structure confirmed that the two metal centers are bridged symmetrically by the iodine atom. As predicted by the 18-electron rule, the complex does not contain an Fe-Fe bond. The cyclopentadienyl groups adopt a trans arrangement presumably to minimize steric repulsion between the rings.

Information on the structure of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2\text{-}(\mu_2\text{-}Br)PF_6$ can be obtained by infrared and NMR spectroscopy and from an additional probe: the asymmetric metal centers. Assuming the general features are similar to those of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2(\mu_2\text{-}I)BF_4$, two possible structures are 19a and 19b. The bridged bromide could

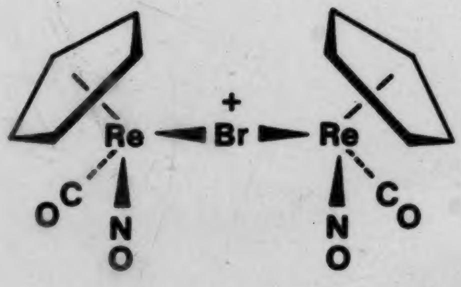


19a-CIS

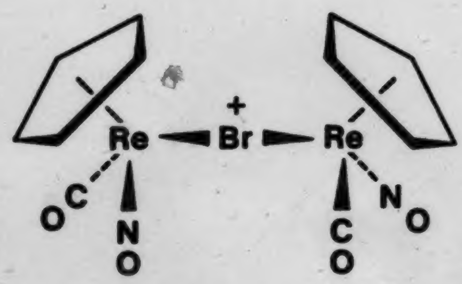


19b-TRANS

exist in solution in a cis or trans form or as a mixture of both these geometric isomers. Because of the presence of two asymmetric centers, two diastereomers are possible for *each* geometric isomer. Structures for the two diastereomers of the cis isomer are shown as 19a-RS and 19a-RR. On steric or electronic grounds there is no obvious difference in the expected stability of diastereomers of the bridged bromide (19). As the compound has been constructed from two separate rhenium units, there is every reason to expect any cis or trans geometric isomers of 19 to form with approximately equal proportions of their two diastereomers.



19a-RS



19a-RR*

In CH_2Cl_2, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$ (19) shows two *symmetric* bands at 2020.0 and 1761.7 cm^{-1}, frequencies consistent with terminal CO and NO stretching modes.

---

[*] Only one enantiomer of the Cis RR/SS diastereomer is shown.

There is no suggestion of shoulders or the near coincidence of two bands. As cis and trans forms would be expected to show different ν(CO) and ν(NO) frequencies, this result suggests 19 exists as only one geometric isomer in CH_2Cl_2* at room temperature. The solid state infrared of 19 in Nujol also shows single bands for the CO and NO ligands; again suggestive of one geometric isomer (cis or trans).

The diastereomers of cis and trans forms of 19 have in principle different infrared spectra. However, the complete resolution of this diastereotopic difference by solution infrared spectroscopy has not been possible for any of the compounds prepared in this study. The very low symmetry of their structures predicts that *each diastereomer of each geometric isomer* of 19 would exhibit two carbonyl and two nitrosyl stretching modes in the infrared. The actual number of peaks observed can, of course be less than that predicted by the symmetry rules.[126] In the case of the bridged bromide only one ν(CO) and one ν(NO) band could be found in dichloromethane or in a Nujol mull.

---

*As CH_2Cl_2 gives somewhat broad peaks it would be of interest to obtain infrared data in other media, unfortunately 19 is cleaved by other solvents of sufficient polarity to dissolve the compound.

Further evidence for the solution structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$ comes from the proton NMR. In CD_2Cl at 200 MHz, the compound shows two $\eta\text{-}C_5H_5$ signals of approximately equal intensity at 6.082 and 6.066 ppm. The spectrum remains constant from -90°C to +60°C. The separation of the cyclopentadienyl signals is typical of diastereomers of the rhenium group (see Section III-C and Chapter V). The approximate 1:1 ratio of these signals and the lack of temperature dependence further suggests they are due to diastereomers of **19** rather than cis and trans geometric isomers.

In summary, the data indicate that $[(\eta\text{-}C_5H_5)Re(CO)\text{-}(NO)]_2(\mu_2\text{-}Br)PF_6$ (**19**) exists in solution and the solid state as two diastereomers of one geometric isomer. From steric arguments, and in analogy to $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2\text{-}(\mu_2\text{-}I)BF_4$, these diastereomers are assigned the trans structure **19**b.

SECTION III

CHEMISTRY OF $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$

The reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) with trityl cation, described in Chapter II, occurs with hydride abstraction, followed by coordination of the rhenium group to triphenylmethane. Strong ligands react with the isolated product, $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ to displace Ph_3CH. In the present chapter, the trityl reaction is used to prepare dinuclear derivatives containing two units of the rhenium group.

A. Preparation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$.

Dropwise addition of a CH_2Cl_2 solution of Ph_3CPF_6 to $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) at room temperature gave initially an orange solution from which rapidly precipitated orange, air stable microcrystals. Infrared monitoring indicated terminal carbonyl and nitrosyl bands with frequencies suggestive of a cation of the rhenium group. ^1H NMR of the product mixture showed Ph_3CH, and cyclopentadienyl signals in the cation region. In addition, peaks consistent with formation of a metal hydride were found at *ca.* -15 ppm. Elemental analysis of the precipitate suggested the new compound be formulated as the dinuclear hydride, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(H)PF_6$ (20) [Eq (55)].

$$2(\eta\text{-}C_5H_5)Re(CO)(NO)H + 1Ph_3CPF_6 \longrightarrow [(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(H)PF_6 + 1Ph_3CH \qquad (55)$$

In the reaction shown in Eq (55), one mole of Ph_3C^+ consumes two moles of the rhenium hydride (5). The first step of this reaction would involve hydride abstraction from one mole of 5. From the studies described in Chapter III, the expected product of this initial step would be one mole of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13). The nature of the rhenium product isolated in 78% yield from Eq (55) suggests the second step is displacement of Ph_3CH from 13 by the second mole of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5). However, in a separate experiment, reaction of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(Ph_3CH)]PF_6$ (13) with 5 resulted in decomposition, with formation of only traces of the dinuclear hydride 20; thus 13 as such cannot be an intermediate in Eq (55). After the initial hydride abstraction step of Eq (55), formation of the dinuclear hydride 20 must occur by a more direct route without the intermediacy of a triphenylmethane complex.

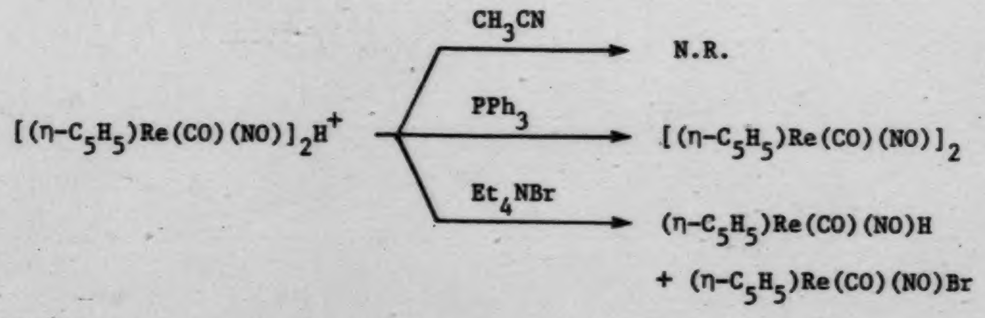
The preparation of dinuclear transition metal hydrides with triphenylmethyl cation has only recently been reported in the literature. In 1978, Beck[87] discovered similar reactions of the trityl cation with $(\eta\text{-}C_5H_5)M(CO)_3H$ (M = Mo, W) afforded the hydrides $[(\eta\text{-}C_5H_5)M(CO)_3)]_2H^+$. Cutler[127] in 1980 reported that reaction of

$(\eta\text{-}C_5H_5)Fe(CO)(L)H$ (L = phosphine) gave phosphine substituted, hydride dimers $[(\eta\text{-}C_5H_5)Fe(CO)(L)]_2H^+$.

B. Reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$.

The hydride $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(H)PF_6$ (20) can be considered a cation of the type $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$, where the ligand L is $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5). The analogous compound 19, where L is $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$, (9) reacts rapidly with nucleophiles to displace the rhenium bromide 9 (see Section II-B). When these same reactions were attempted with the dinuclear hydride 20 very different results were obtained. The reactions of 20 are shown in Scheme 16; the rhenium products, all of which have been prepared separately in this study were identified by infrared and ^1H NMR spectroscopy.

Scheme 16:



The dinuclear hydride 20 readily dissolves in acetonitrile to give orange solutions with infrared and

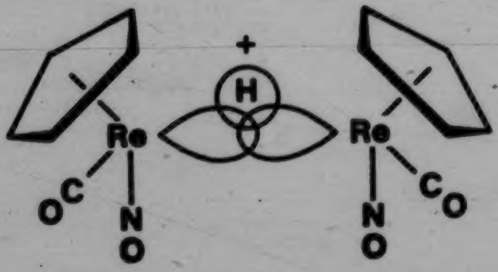
^{1}H NMR spectra similar to those recorded in other solvents. There is no evidence for displacement products as were obtained with $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)^+$. The hydride $\underset{\sim}{20}$ does react with Ph_3P, but to give the deprotonation product, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$*. This reaction suggests, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2H^+$ is a Lowry-Bronsted acid, capable of donating a proton to the base PPh_3. Only with the anionic nucleophile Et_4NBr was a displacement reaction of $\underset{\sim}{20}$ observed. The weakly basic Br^- cleaves $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2H^+$ to give a 1:1 mixture of the mononuclear hydride $\underset{\sim}{5}$ and the bromide $\underset{\sim}{9}$.

These reactions reflect a fundamental difference in the bonding modes of the bridged bromide $\underset{\sim}{19}$ and the hydride $\underset{\sim}{20}$. The 18-electron rule as applied to the $CpRe(CO)(NO)^+$ fragment requires a two-electron donor ligand. One of the lone pairs on the bromine atom of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ ($\underset{\sim}{9}$) can provide these electrons as suggested by the resonance forms of $\underset{\sim}{19}$. The reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}Br)PF_6$ ($\underset{\sim}{19}$) occur as expected with displacement of this weak donor by more strongly coordinating ligands. The rhenium hydride $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$) does not have a similar lone pair of electrons on hydrogen and thus cannot form two-electron bonds in this fashion.

---

*The chemistry of the rhenium dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ is discussed in Section IV.

The bonding in $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(H)PF_6$ (20) is probably best described as a closed, three-center, two-electron molecular orbital. Overlap of a vacant sigma type orbital on the $CpRe(CO)(NO)^+$ fragment with the two orbitals of the rhenium hydride bond in $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) would provide three new molecular orbitals. The low energy bonding MO would be occupied by the two-electrons, originally contained in the rhenium hydride bond of (5). In such a bridging complex there is a bonding interaction of the hydride with each metal *and* between the two metal centers.



The presence of a metal-metal bond in $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) would explain the failure to to observe cleavage reactions with neutral donor ligands. An alternate route of reaction, deprotonation, becomes available with ligands of sufficient basicity. A bridging hydride structure for 20 could best be confirmed by a crystal study. There is some evidence[60] that the

NMR resonance of a hydride bridging two or more metals will occur at higher fields than a terminal hydrogen. This is certainly consistent with the bonding proposed for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ ($\underset{\sim}{20}$). The hydride resonance in this complex has been shifted *ca.* 7 ppm *upfield* from its position (-8.50 δ) in the mononuclear hydride $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ ($\underset{\sim}{5}$).

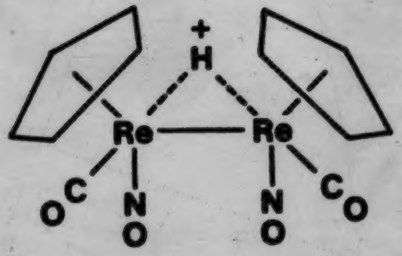
The bonding in hydride bridged dinuclear complexes was first described by Doedens and Dahl[128] in 1965. The original scheme provided for bonding only between the hydride and the two metal centers (i.e., an *open*, two-electron, three-center bond). The greater numbers of higher quality structural studies now available suggest bridging hydrides are best described by *closed*, two-electron, three-center bonds with some metal-metal bonding.[114,115]

C. The Structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$.

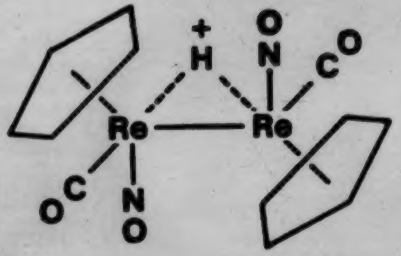
Despite the intense study of hydride bridged metal complexes, little structural information is available on such compounds containing π-cyclopentadienyl ligands. Analysis of the infrared spectra of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2\text{-}(\mu_2\text{-}H)^+$ in an attempt to obtain structural information was reported by Symon and Waddington[129] in 1971. After excluding impurity peaks, only two carbonyl bands were found for the iron complex. This is consistent with the presence of one cyclopentadienyl peak in the ^{1}H NMR and was assigned to a centrosymmetric structure with trans Cp rings. The spectroscopic data which has been reported for $[(\eta\text{-}C_5H_5)M(CO)_2]_2(\mu_2\text{-}H)^+$ [110] (M = Mo, W)[86] would also be consistent with the presence of only trans isomers. Recently, Gray[110] reported protonation of the monophosphite analog of the iron dimer to give $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3\text{-}P(OCH_3)_3(H)]X$ ($X = BF_4^-$, PF_6^-). The ^{1}H NMR data of both these compounds and the infrared of the BF_4^- complex suggested only one geometric isomer was formed. The solid state infrared spectrum of the PF_6^- salt shows extra ν(CO) bands which the authors attributed to a mixture of cis and trans isomers.

The crystal structure of a related hydride complex, $(\eta\text{-}C_5H_5)_2Mo_2(H)(PMe_2)(CO)_4$ was reported in 1965.[128] The molybdenum compound contains bridging hydride and PMe_2 groups with terminal carbonyls and trans cyclopentadienyl ligands. This structure was confirmed and the exact hydrogen position located in a later neutron diffraction study.[114] The molecule has a bent Mo-H-Mo arrangement consistent with a closed, three-center, two-electron bond.

A similar bridging hydride structure for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (**20**), could have a cis (**20a**) or trans (**20b**) configuration. Two diastereomers are possible for each of these geometric isomers. As



20a

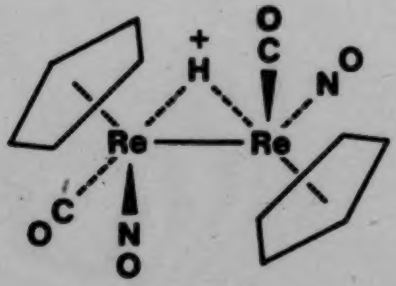


20b

with the bridged bromide dimer 19, diastereomers would be expected to form in roughly equal amounts.

The 400 MHz, ^1H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) in CD_2Cl_2 has cyclopentadienyl resonances at 6.040 (10H) and 6.033 (10H) ppm. Peaks assigned to bridging hydride ligands occur at -15.315 (1H) and -15.609 (1H) ppm. The spectrum was unchanged from -90°C to +60°C. The small chemical shift difference between the cyclopentadienyl signals (0.007 ppm) suggests they are due to two diastereomers. There was no change in the ratio of these peaks when the ^1H NMR was recorded in the more polar solvent CD_3CN as would be expected for geometric isomers. These observations and the lack of temperature dependence of the ^1H NMR suggests $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2\text{-}(\mu_2\text{-}H)PF_6$ (20) exists in solution as two diastereomers of one geometric isomer; presumably the less sterically hindered trans structure 20b.

The infrared spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) in CH_2Cl_2 is shown in Figure IV. The two partly overlapping bands at 2023 and 2013 cm^{-1} suggest terminal carbonyl ligands. In the terminal nitrosyl region, there is a broad band at 1756 cm^{-1}, probably due to two unresolved peaks. Prediction of the number of infrared bands expected for 20 is rather difficult due to the presence of diastereomers and the lack of exact structural data. For example, if the hydride ligand in the enantiomer of the trans form shown in 20b-RS were located exactly between



20b-RS

the rhenium atoms, the molecule would have C_i symmetry and one band would be predicted for the CO(NO) ligands. If the hydride ligand were located off-center, the symmetry would be reduced to C_1 and two CO(NO) bands are expected. The situation is further complicated as the symmetry rules only predict the *maximum* number of

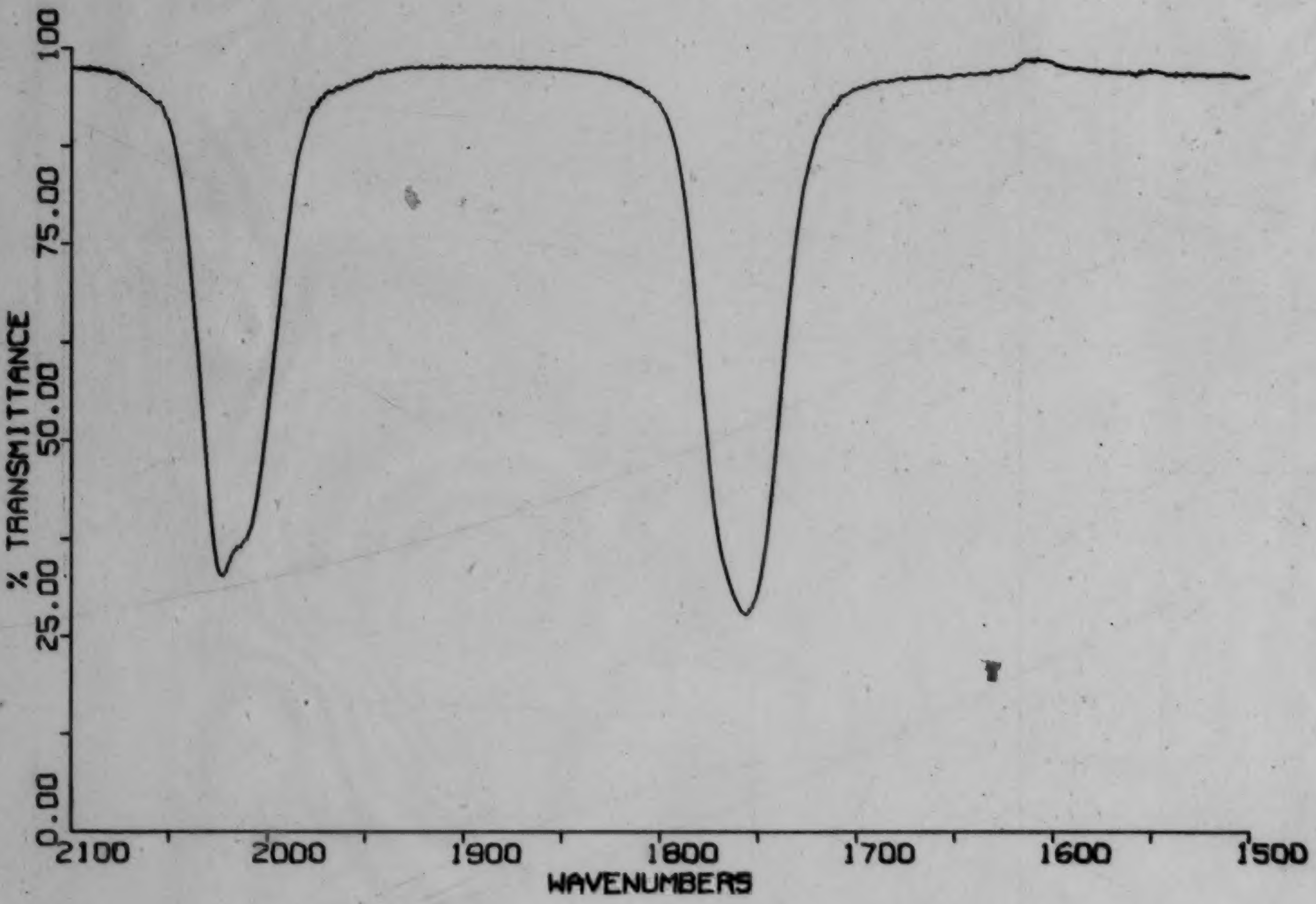


FIGURE IV. Infrared Spectrum of $[(\eta-C_5H_5)Re(CO)(NO)]_2(\mu_2-H)PF_6$, CH_2Cl_2.

bands that may be observed.

The intensity of the infrared bands for $[(\eta\text{-}C_5H_5)\text{-}Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) do not change in the more polar solvent CH_3CN, as would be expected for geometric isomers. This observation, in conjunction with the NMR data, suggests these peaks are due to two diastereomers of the trans geometric isomer 20b.

The infrared spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) in Nujol shows four carbonyl bands and four partially resolved nitrosyl peaks all of approximately equal intensity. The extra bands could suggest (20) in contrast to the solution structures exists in the solid state as comparable amounts of cis and trans isomers. Alternatively depending upon their exact structures this infrared data could still be consistent with two diastereomers of the trans geometric isomer. Perhaps the difference in the infrared spectra of diastereomers is emphasized in the solid state. Experiments are presently in progress to grow X-ray quality crystals of 20. Further information on the structure of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (20) will have to await an X-ray study.

SECTION IV

THE CHEMISTRY OF $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$

In Section III it was noted that one of the reaction modes of the bridged hydride, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (**20**) was deprotonation. This reaction provides an excellent route to the long sought metal carbonyl dimer, $[(\eta\text{-}C_5H_5)\text{-}Re(CO)(NO)]_2$.

A. Preparation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$.

Addition of Et_3N to a suspension of $[(\eta\text{-}C_5H_5)Re(CO)\text{-}(NO)]_2(\mu_2\text{-}H)PF_6$ (**20**) in CH_2Cl_2 gave initially a red solution from which precipitated reddish-black crystals.

Mass spectrum and elemental analysis showed this material to be the rhenium dimer $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (**21**) [Eq (56)]. The infrared and NMR spectra of **21**

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)^+ \xrightarrow{Et_3N} [(\eta\text{-}C_5H_5)Re(CO)(NO)]_2 \qquad (56)$$

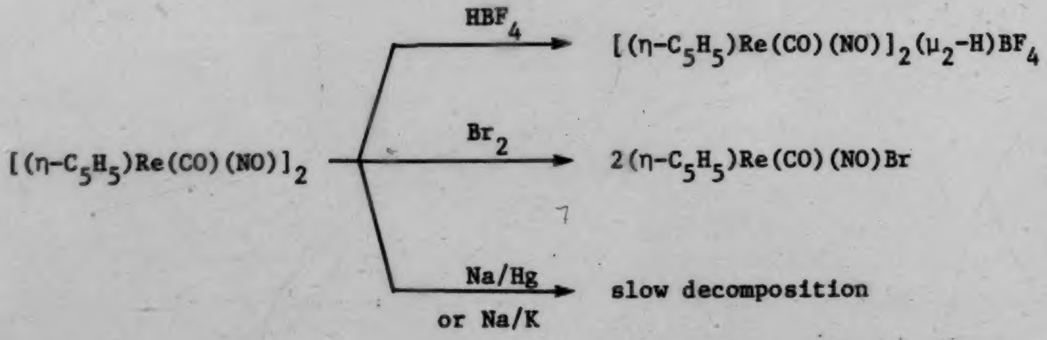
(see Section IV-C) are consistent with this formulation. As with other derivatives of the rhenium group, the dimer shows remarkable air and thermal stability [MP 220°C (dec.)]. The compound is insoluble in hexane; in solvents such as acetone or acetonitrile, its solubility is limited and highly temperature dependent. The reaction of the bridged hydride 20 with Et_3N [Eq (56)] provides a convenient and high yield route for the preparation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21). If necessary the initial product can be further purified by column chromatography or recrystallization.

It is interesting to note that the original investigation of the chemistry of $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]BF_4$ (1) by Graham, *et al.*[12] was in search of the rhenium dimer $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21). Synthetic routes which had provided the corresponding manganese dimer were unsuccessful in the rhenium system because of the thermal stability of intermediates. However, in one thermal reaction of triethylamine with the carbonyl cation 1, N. Okamoto[130] was able to isolate *ca.* 50 mg of a black crystalline material, on which he obtained infrared, ^1H NMR and mass spectral data. Unfortunately, Okamoto was never able to repeat this preparation. Comparison of spectroscopic data of the Okamoto product, with that now available for 21 shows that his compound was indeed the rhenium dimer $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$.

C. Reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$.

Application of the 18-electron rule to $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ 21, predicts the rhenium dimer should contain a two-electron metal-metal bond. Such a compound was expected to undergo reactions involving electrophilic attack on this electron-rich bond, followed in some cases by loss of the metal-metal interaction. The reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ ($\underset{\sim}{21}$) shown in Scheme 17, include

Scheme 17:



examples of both these processes. Details of these reactions may be found in the Experimental, Section V.

The Lowry-Bronsted acidity of the bridged hydride, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ ($\underset{\sim}{20}$) was described in Section II-B. The hydride is a relatively strong H^+ source, protonating such weak bases as Et_3N, H_2O, PMe_2Ph, PPh_3, and acetone. This reaction is readily reversible [Eq (57)]; the conjugate base, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ can

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2H^+ \rightleftharpoons [(\eta\text{-}C_5H_5)Re(CO)(NO)]_2 + H^+ \tag{57}$$

be protonated with the strong acid HBF_4/Et_2O, to regenerate the bridged hydride $\underset{\sim}{20}$ as the BF_4^- salt. This reaction confirms that the metal-metal bond of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21) is an area of relatively high electron density, readily attacked by electrophiles. Similar protonations of metal carbonyl-η-cyclopentadienyl dimers with strong acids have been reported for the Group VIb and iron group compounds, $[(\eta\text{-}C_5H_5)M(CO)_X]_2$ (X = 3, M = Mo, W;[86] X = 2, M = Fe,[86] Ru[110]).

Another common reaction of metal carbonyl dimers is cleavage by halogens to give the corresponding mononuclear halides. The rhenium dimer 21 reacts readily with bromine at low temperatures, but the reaction mixture must be heated to give the final product $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9). Infrared monitoring shows the initial product of this reaction to be a species similar to the bridged bromide, $[(\eta\text{-}C_5H_5)Re(CO)(NO)](\mu_2\text{-}Br)^+$ (19). This suggests the initial step of bromination is electrophilic attack on the Re-Re bond of 21 to give $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2\text{-}(\mu_2\text{-}Br)^+Br^-$. At higher temperatures, the bromide counter ion cleaves the bridged dimer to give two moles of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9). A model for the second step of this process is provided by the reaction of the bridged bromide 19 with Et_4NBr; shown in Scheme 15. A similar mechanism to that described above has been suggested for the halogenation of the iron dimer, $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$.[112,131]

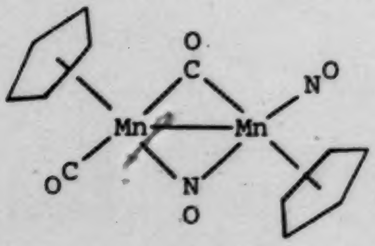
In Chapter III, it was noted that attempts to prepare the anion $(\eta\text{-}C_5H_5)Re(CO)(NO)^-$ from $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5)

had been frustrated by the non-acidity of the hydride. Another commonly used method[80,107] for the preparation of carbonyl-η-cyclopentadienyl metal anions involves the reduction of the metal-metal bond of the corresponding dimers. All attempts to reduce the rhenium dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ ($\underset{\sim}{21}$) with sodium amalgam or sodium-potassium alloy gave only slow decomposition to non-carbonyl containing products. Similar results were obtained in the reduction of the bromide, $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ ($\underset{\sim}{9}$). Apparently the anion either does not form in these reactions or has very low stability. The failure to prepare $(\eta\text{-}C_5H_5)Re(CO)(NO)^-$ by these routes is surprising, and an explanation is not apparent.

C. The Structure of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$.

Stereochemical nonrigidity in dinuclear metal carbonyl-η-cyclopentadienyl complexes is one of the more intensively studied subjects of organotransition metal chemistry. The variety of structural forms exhibited by the iron dimer $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ is typical of this class of compounds as a whole. It was assumed that spectroscopic studies would detect similar behavior for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ $\underset{\sim}{21}$. The complexity of infrared and NMR results obtained for the rhenium dimer surpassed all expectations. Before discussing this data, the behavior of the analogous manganese dimer will be discussed.

A detailed study, including the crystal structure of $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ was published in 1973 by Ibers, Marks, and co-workers.[123] In the solid state the manganese dimer was suggested to have a trans structure with mixed CO and NO bridging ligands. In solution the compound exists as a mixture of cis and trans bridged forms believed to be in equilibrium with small amounts of nonbridged species. The concentration of putative cis and trans nonbridged forms is too low to be detected spectroscopically. There is no evidence in the case of the manganese dimer for structures containing two CO or two NO bridging ligands.



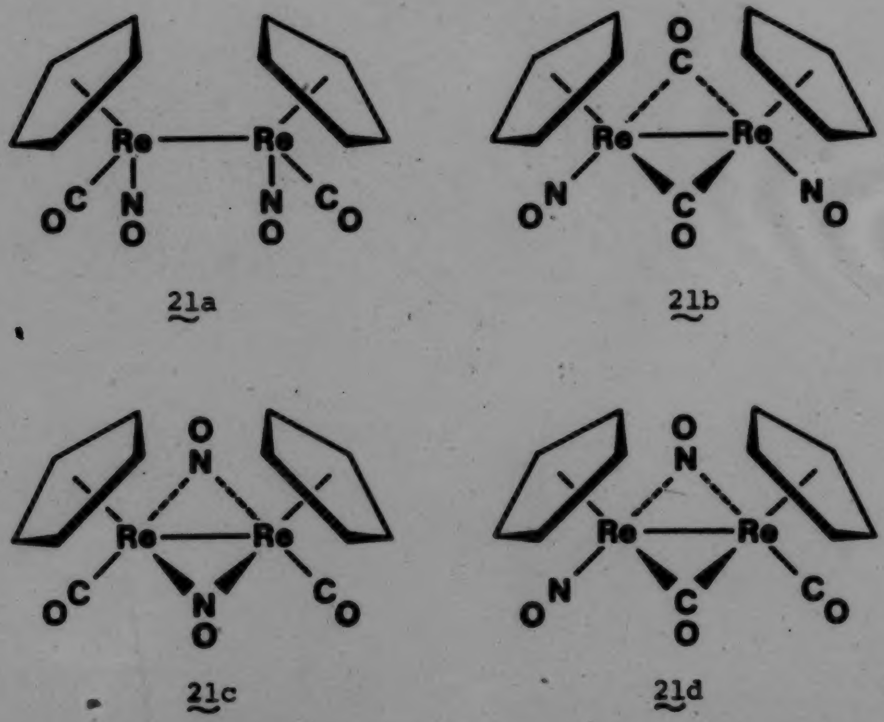
The limiting low temperature (-62°C) ^1H NMR spectrum of $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ shows two doublets separated by *ca.* 0.23 ppm. Each doublet is due to two chemically nonequivalent cyclopentadienyl rings on the mixed bridged forms. The more abundant low field doublet was assigned to the trans isomer; the other doublet is due to the cis form. The cis and trans mixed bridged structures are also readily distinguished by infrared spectroscopy. The ratio of cis to trans forms was found to increase with the polarity of the solvent. On warming the two doublets coalesced to one sharp signal above *ca.* 40°C. These NMR changes were attributed to bridge-terminal exchange of the CO and NO ligands, followed by rotation about the Mn-Mn bond in nonbridged forms.

The observation of a single sharp line in the high temperature limit for $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$ was quite unexpected. The presence of two asymmetric metal centers creates diastereomers for each of the cis and trans nonbridged forms. Thus, even if cis-trans exchange is occuring rapidly on the NMR time scale the high temperature spectrum should still show two cyclopentadienyl signals for the two distinct diastereomers. Perhaps one of the most reasonable explanations suggested for this result was a rapid inversion of the configuration at the metal centers in the high temperature limit. Racemization would equilibrate diastereomers, giving one averaged cyclopentadienyl signal for all the structural forms of $[(\eta\text{-}C_5H_5)Mn(CO)(NO)]_2$. It was hoped that the detailed information available for the manganese system would aid elucidation of any similar processes occuring with $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (**21**).

* * * * *

There are a large number of structures one could draw for a compound with the formula $[(\eta\text{-}C_5H_5)_2Re_2(CO)_2(NO)_2]$. Eliminating chemically unreasonable species and utilizing only forms for which there is precedent in the literature, four structural types are possible for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (**21**). These structures are shown in Scheme 18. Included are the nonbridged **21a** and the mixed CO/NO bridged structures **21d** suggested for the manganese dimer. Symmetrically

Scheme 18: Possible structural types for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. Only the cis isomers are shown.

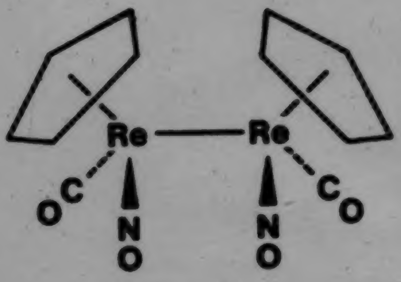


21a **21b**

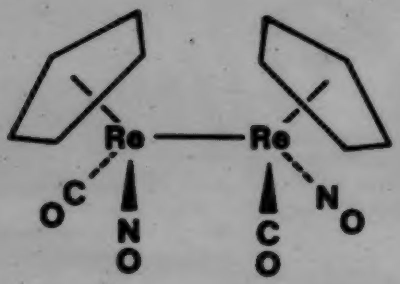
21c **21d**

bridged forms containing two terminal CO 21b or NO 21c ligands must also be considered for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. Only the cis isomers are shown in Scheme 18, but each structural type could also have a trans geometric isomer.

In addition to the four structural types each with two geometric isomers, there is also the possibility of optical isomers. The unbridged forms contain two asymmetric metal centers. The cis and trans isomers would *each* exist as a pair of diastereomers. Structures for the two cis, nonbridged diastereomers are shown as 21a-RS and 21a-RR.* These diastereomers are different compounds and should be distinguishable by spectroscopic methods. The cis and trans isomers of the mixed bridged structure 21d would *each* exist as two enantiomers. The enantiomers would be indistinguishable by infrared or NMR spectroscopy. The cis and trans isomers of the



21a-RS



21a-RR

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[*] Only one of the two enantiomers of the RR/SS diastereomer is shown.

symmetrically bridged forms **21b** and **21c** would not show optical isomers.

In total, there are ten distinct structures possible for the rhenium dimer: cis and trans nonbridged, each with two diastereomers; cis and trans mixed CO/NO bridged; cis and trans bridging CO's; cis and trans bridging NO's. The solid state and solution structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ **21**, could exhibit some or all of these forms. From previous studies and the results presented in Sections II-C and III-C, all ten possible structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ would in principle be distinguishable by a combination of infrared and NMR spectroscopy.

* * * * *

The infrared spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (**21**) in CH_2Cl_2 is shown in Figure V. The rhenium dimer has strong bands consistent with terminal carbonyls at 1955.5 and 1931.5 cm^{-1} and terminal nitrosyls at 1675 (distinct shoulder) and 1668 cm^{-1}. The medium peak at 1727.0 cm^{-1} and the smaller one at 1605.5 cm^{-1} are probably due to bridged CO and NO ligands, respectively. This spectrum is consistent with the various structures discussed above for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (**21**). The number of peaks and their relative intensities suggest a variety of structures

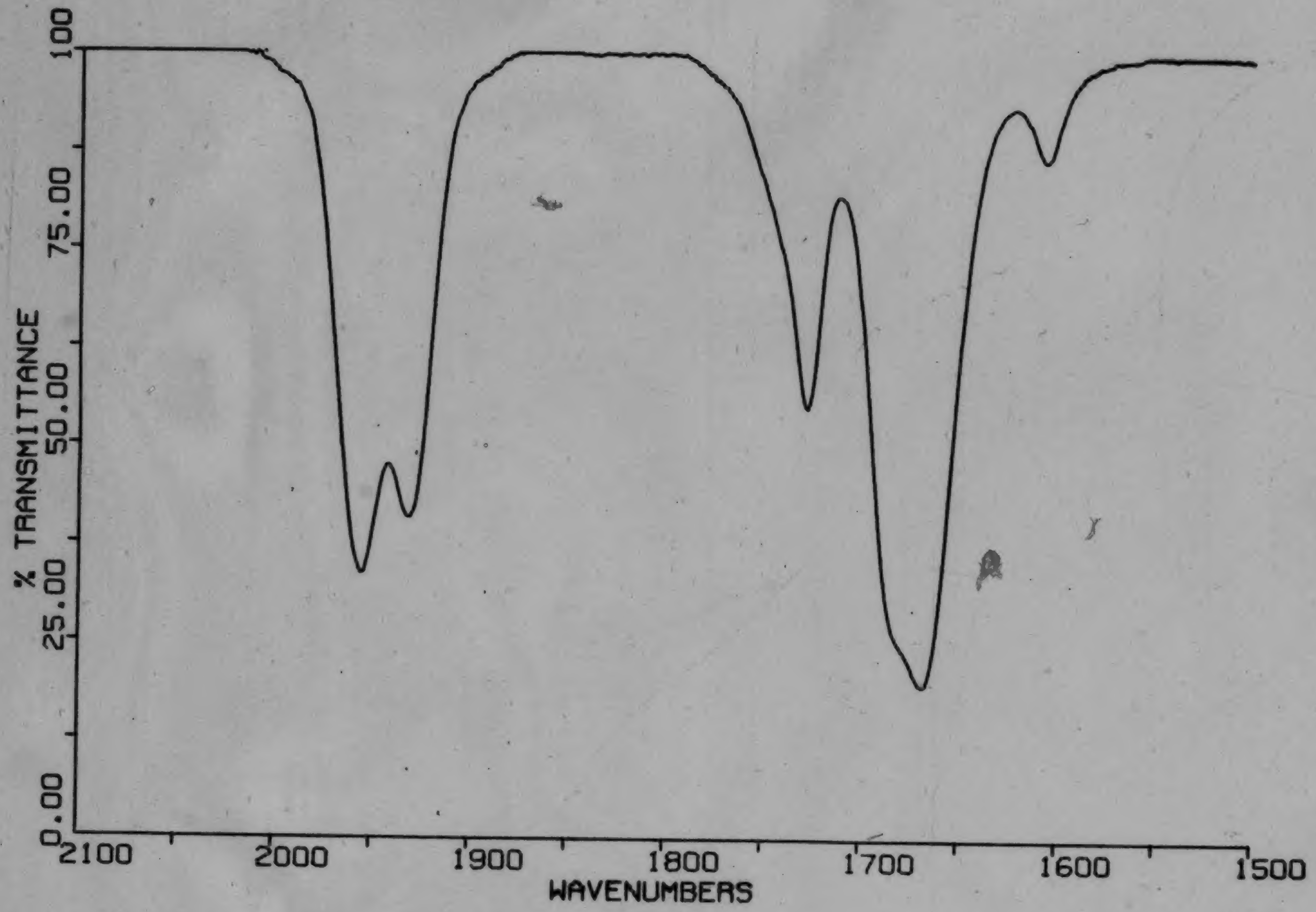

FIGURE V. Infrared Spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$, CH_2Cl_2.

are present. In contrast to the manganese analog, the rhenium dimer has a preponderance of forms containing only terminal CO and NO ligands. As was found with the iron group dimers the tendency to form bridging structures decreases with the heavier metal.

The insolubility of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ ($\underset{\sim}{21}$) in hexane severely limits the amount of information obtainable by infrared spectroscopy. In other solvents* the rhenium dimer shows the same basic features as Figure V with slight changes in the ratio of peaks. The intensity of the highest frequency terminal CO and NO bands increase with solvent polarity. This behavior is similar to the manganese dimer and suggests the bands at 1955.5 and 1675 cm^{-1} are mainly due to cis structures.

The variable temperature 200 MHz, ^1H NMR spectra of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ ($\underset{\sim}{21}$) is shown in Figure VI. In THF-d_8 at -120°C, the rhenium dimer shows *eight* distinct cyclopentadienyl signals between 5.6 and 5.9 ppm. On warming, these signals coalesce, by a complex series of changes to give ultimately a single broad peak at *ca.* +100°C. To obtain the limiting high temperature spectrum it was necessary to change the solvent to DMSO-d_6. At +120°C, the rhenium dimer shows one sharp Cp signal at

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*Infrared data was also obtained in benzene, toluene, chloroform, THF, acetone, acetonitrile, nitromethane and dimethylsulfoxide.

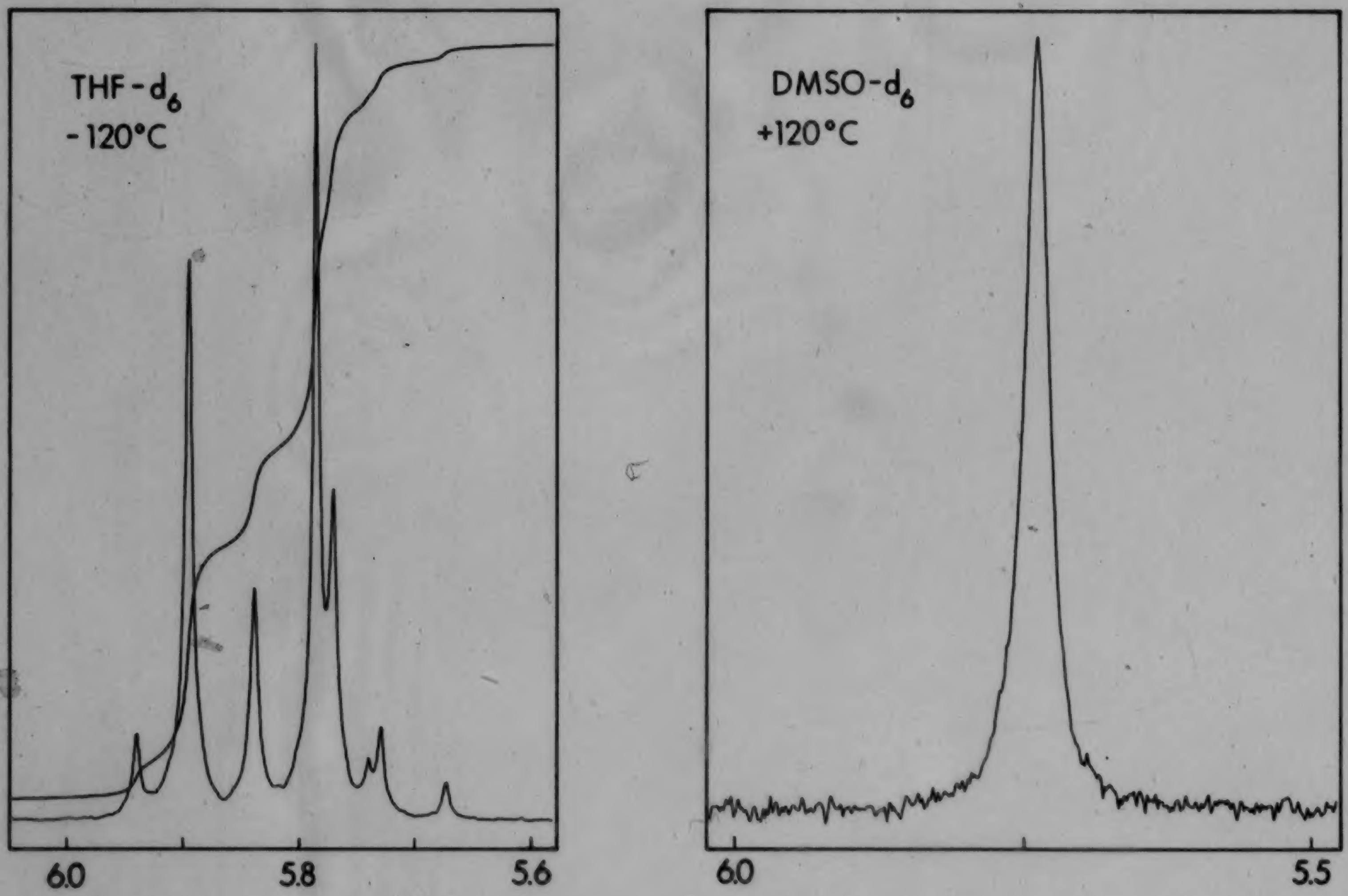


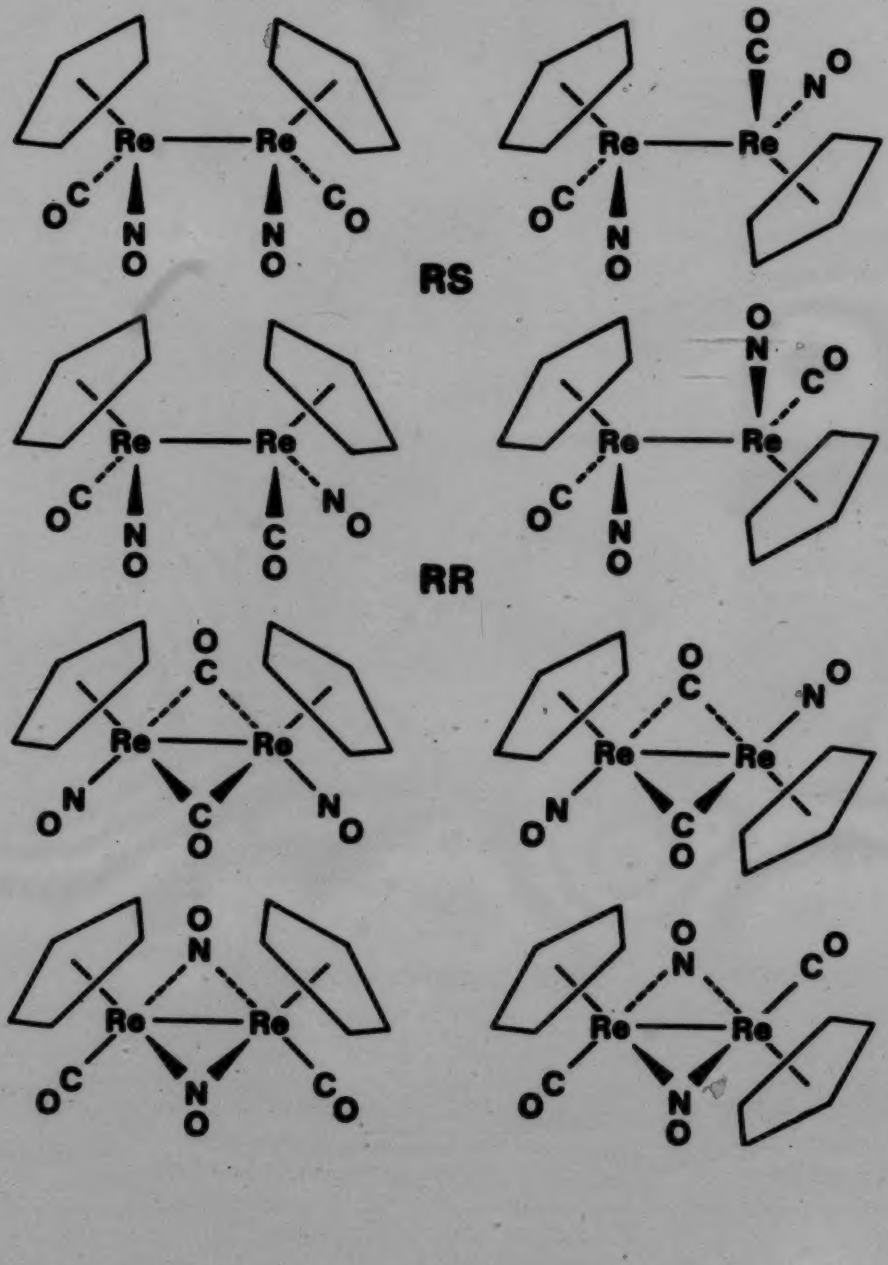
FIGURE VI. ^{1}H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$, 200 MHz.

5.975 ppm (Figure VI). The latter observation suggests that at this temperature, interconversion of all structures is occurring rapidly on the NMR time scale by a process(es) which results in racemization at rhenium.

The low temperature spectrum of 21 (Figure VI), shows eight Cp signals of unequal intensity. The possible structures discussed for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21) each contain chemically equivalent cyclopentadienyl rings with the exception of the mixed CO/NO bridged species 20d. As the manganese study demonstrated, each mixed bridged geometric isomer would show a 1:1 doublet in the low temperature limit. The complete absence of any two peaks of equal intensity that could be identified as a 1:1 doublet of this type in the THF-d_8 spectrum of Figure VI rules out these forms as possible structures for $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. Replacement of Mn for the heavier rhenium atoms in the $[(\eta\text{-}C_5H_5)M(CO)(NO)]_2$ system has greatly changed the relative stabilities of possible structures.

Elimination of the two mixed CO/NO bridged geometric isomers leaves eight physically distinct structures for the rhenium dimer. These eight structures are shown in Scheme 19; each would show one η-cyclopentadienyl resonance. The eight peaks obtained in the low temperature limiting spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ 21 are attributed to

Scheme 19: The probable structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. Only one enantiomer is shown for the RR/SS diastereomer.



these eight isomers. It is proposed that the eight structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21) are interchanged at higher temperatures by three processes: (1) bridge-terminal exchange of CO/NO ligands, (2) cis-trans isomerization *via* rotation about the Re-Re bonds in the nonbridged structures, and (3) racemization at the metal center(s).

Without further information, the exact assignment of these processes to the line shape changes in the ^1H NMR of 21 becomes very speculative. It was hoped that ^{13}C NMR could be correlated with the proton results. The insolubility of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21) has thus far prevented the acquisition of good carbon NMR data even at room temperature. Other experiments on the rhenium dimer are still in progress. Crystals of 21 have been submitted for X-ray analysis and hopefully the solid state structure(s) will soon be available. The use of variable temperature infrared spectroscopy may provide information on the instaneous solution structures of the rhenium dimer. Derivatives such as $[(\eta\text{-}Me_5C_5)Re(CO)(NO)]_2$ and $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)]_2$ might give spectroscopic data much less complex than that of 21. These studies could shed further light on the $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ system. Whatever the results of future studies, the rhenium dimer $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ provides one of the most striking and challenging examples of stereochemical nonrigidity in organotransition metal chemistry.

SECTION V

EXPERIMENTAL

Preparation of $[(\eta-C_5H_5)Re(CO)(NO)]_2(\mu_2-Br)PF_6$ (19).

Trimethyloxonium hexafluorophosphate (0.026 g, 0.13 mmol) and $(\eta-C_5H_5)Re(CO)(NO)Br$ (0.10 g, 0.26 mmol) were stirred in 10 mL of CH_2Cl_2 for 8 hr at room temperature. After filtering, the addition of diethyl ether gave a precipitate which was collected and washed with 3 x 5 mL of ether to give orange microcrystals of the brominated dimer (19), 0.042 g, 38% yield.

Characterization: IR and proton NMR (see Discussion). Anal. Calcd for $C_{12}H_{10}Re_2O_4N_2BrPF_6$: C, 17.09; H, 1.19; N, 3.32. Found: C, 17.02; H, 1.16; N, 3.40.

Preparation of $[(\eta-C_5H_5)Re(CO)(NO)]_2(\mu_2-H)PF_6$ (20).

Triphenylcarbenium hexafluorophosphate (1.25 g, 3.22 mmol) dissolved in 10 mL of CH_2Cl_2 was added dropwise to a solution of $(\eta-C_5H_5)Re(CO)(NO)H$ (2.00 g, 6.44 mmol) in 5 mL of CH_2Cl_2 at room temperature. The solution turned orange and an orange precipitate appeared. The solvent was syringed away and the precipitate washed with 2 x 5 mL of CH_2Cl_2 to give orange microcrystals of the protonated dimer (20), 1.92 g, 78% yield.

Characterization: IR and proton NMR (see Discussion). Anal. Calcd for $C_{12}H_{11}ReO_2NPF_6$: C, 18.85; H, 1.45; N, 3.66. Found: C, 18.70; H, 1.44; N, 3.64.

Preparation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (21).

Triethylamine (15.0 mL, 107.85 mmol) was added dropwise to a suspension of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)PF_6$ (2.00 g, 2.62 mmol) in 30 mL of CH_2Cl_2 at room temperature. As the starting material dissolved the solution became dark red and a reddish-black precipitate appeared. The solvent was removed under reduced pressure to give a black residue. This material was chromatographed on an Aluminium oxide (neutral) column with $CHCl_3$ affording reddish-black crystals of the dimer (21), 1.50 g, 93% yield, MP 220°C (dec.).

Characterization: IR and proton NMR (see Discussion). Mass spectrum, 125°C/14 ev: $[Cp_2Re_2(CO)_2(NO)_2]^+$, $[Cp_2Re_2(CO)(NO)_2]^+$. Anal. Calcd for $C_{12}H_{10}Re_2O_4N_2$: C, 23.30; H, 1.63; N, 4.53. Found: C, 23.38; H, 1.60; N, 4.53.

Reactions of $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$:

(a) Bromination:

Bromine (0.025 mL, 0.48 mmole) was added dropwise to $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$ (0.2 g, 0.32 mmol) in 10 mL of CH_2Cl_2

at 0°C. After refluxing the solution for 2 hr at 50°C, solvent was removed under reduced pressure to give a red solid. This material was chromatographed with benzene on Florisil (100-200 mesh) to give red crystals of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9), 0.17 g, 68% yield. The bromide was identified by comparison of its infrared, NMR and mass spectra to authentic samples.

(b) Protonation with HBF_4/Et_2O:

The rhenium dimer $\underset{\sim}{21}$ (0.10 g, 0.16 mmol) was dissolved in 10 mL of methylene chloride at room temperature forming a dark red solution. Addition of HBF_4/Et_2O produced an orange solution from which precipitated an orange solid. Diethyl ether (20 mL) was added to complete precipitation. The solid was collected, washed with 3 x 10 mL of ether and dried *in vacuo* (0.109 g, 96% yield). Infrared and proton NMR spectroscopy showed this material to be $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2(\mu_2\text{-}H)BF_4$.

CHAPTER V

CYCLOPOLYENE AND CYCLOPOLYENYL PRODUCTS OF THE RHENIUM GROUP

SECTION I

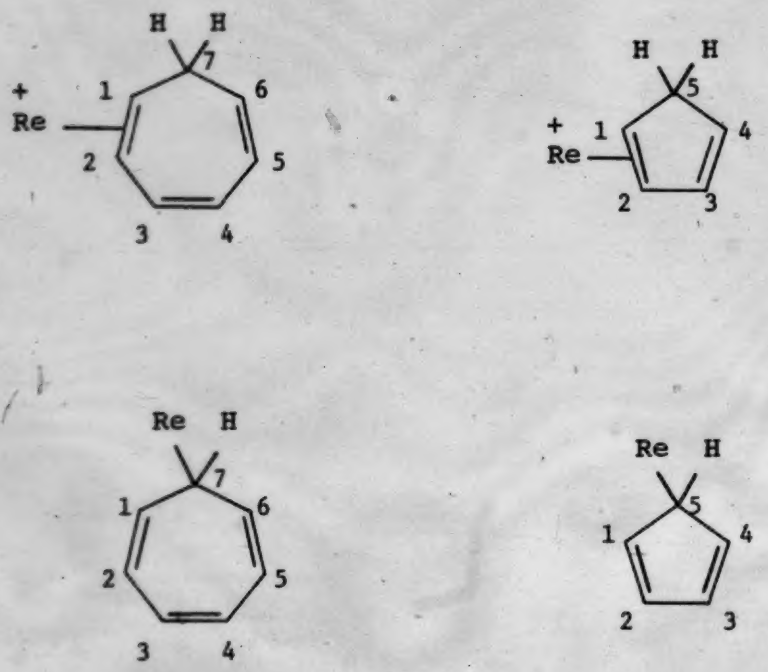
INTRODUCTION

In this chapter the chemistry of some compounds in which the rhenium group is bonded to cyclopolyene and cyclopolyenyl ligands will be discussed. The specific organic ligands which have been used are cyclopentadiene and cycloheptatriene. The study of these complexes has focused on their reactions and the structures they exhibit in solution.

A. The Interconversion of Sigma and π Structures.

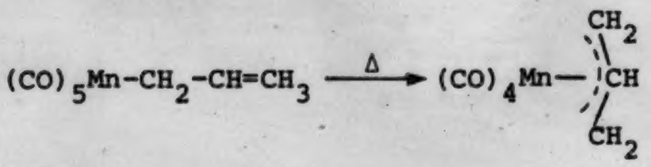
The requirements of the 18-electron rule as applied to the rhenium group, $(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}$, provide two possible bonding modes with ligands derived from cyclopentadiene or cycloheptatriene. In the first, the metal center can be bonded to one of the double bonds of the C_5H_6 or C_7H_8 molecule to form cationic *cyclopolyene* species, $[(\eta\text{-}C_5H_5)Re(CO)(NO)L]^+$, L = C_5H_6, C_7H_8. In these complexes the rhenium group is η^2-bonded to the 1,2 double bond (Scheme 20). In the second, the metal can replace one of the methylene hydrogens of C_5H_6 or C_7H_8 forming neutral η^1-*cyclopolyenyl* derivatives $(\eta\text{-}C_5H_5)Re(CO)(NO)(\eta^1\text{-}R)$, R = C_5H_5, C_7H_7 (Scheme 20). In such compounds the rhenium group is sigma bonded to the aliphatic carbon $C_5(C_5H_5)$ or $C_7(C_7H_7)$.

Scheme 20: Re = $(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}$

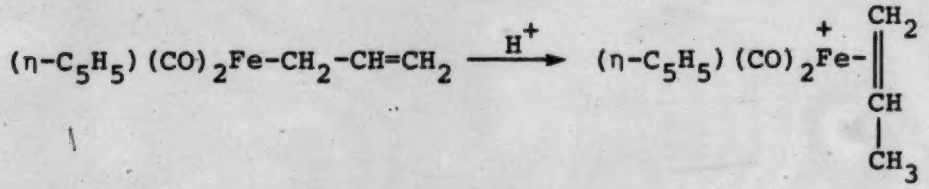


Much of the work discussed in this chapter involves the interconversion of sigma and π structures. There are two very different types of σ-π rearrangements[132] with relevance to this study. Somewhat similar examples of both these reaction modes can be found in the chemistry of metal allyl complexes.

The monohaptoallyl group $M\text{-}CH_2\text{-}CH\text{=}CH_2$ can be converted to a π-acid ligand by either of the reactions shown in Eqs (58) and (59). In the first example [Eq (58)], a monohapto ligand is converted to a species of higher hapticity. For the σ-allyl, $(CO)_5Mn(\eta^1\text{-}C_3H_5)$[133] this can



$$(CO)_5Mn{-}CH_2{-}CH{=}CH_3 \xrightarrow{\Delta} (CO)_4Mn{-}\begin{array}{c}CH_2\\ CH\\ CH_2\end{array} \qquad (58)$$



$$(\eta\text{-}C_5H_5)(CO)_2Fe{-}CH_2{-}CH{=}CH_2 \xrightarrow{H^+} (\eta\text{-}C_5H_5)(CO)_2\overset{+}{Fe}{-}\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_3\end{array} \qquad (59)$$

be accomplished by heating the compound. As the starting material is an 18-electron complex such a rearrangement likely involves prior dissociation of carbon monoxide. Sigma-π conversions of this type may occur thermally or be induced photochemically. Although such reactions were not extensively investigated in the present study, it appears the non-lability of the ligands bonded to rhenium inhibits a similar process for the η^1-cyclopolyenyl complexes of Scheme 20.

A different kind of σ-π rearrangement is shown in Eq (59). In this example the σ-allyl, $(\eta\text{-}C_5H_5)Fe(CO)_2\text{-}(\eta^1\text{-}C_3H_5)$[134] is converted to an η^2-propene cation by reaction with the electrophile H^+. The protonation of various iron η^1-allyl complexes was studied by Green[134] in the early 1960's. More recently Rosenblum[135] has examined similar reactions of transition metal η^1-allyl compounds with electrophiles other than H^+ and discussed their potential use in organic synthesis.

In this thesis, $\eta^1 \rightarrow \eta^2$ and $\eta^2 \rightarrow \eta^1$ conversions have been explored for the complexes shown in Scheme 20. NMR has played a key role in structural determinations. Before turning to the details of this work some background will be presented on the fluxional properties of η^1-cylcopolyenyl compounds.

B. Fluxional η^1-Cyclopolyenyl Compounds of the Transition Metals.

Transition metal η^1-cyclopolyenyl compounds have been intensively studied for nearly 25 years. The interest in such complexes is due to their nonrigid behavior. In solution these compounds are often fluxional *via* intramolecular rearrangements in which the metal center migrates about the cyclopolyenyl ring. In certain cases this motion can be detected by NMR spectroscopy and the pathway by which the metal migrates determined.

The majority of fluxional transition metal η^1-cyclopolyenyl complexes contain the cyclopentadienyl ligand. The first example of such a species, $(\eta\text{-}C_5H_5)Fe(CO)_2(C_5H_5)$ was reported by Piper and Wilkinson[80] in 1956. A reasonable structure based on the 18-electron rule and the properties of other alkyl derivatives of this iron group would contain one pentahapto- and one monohapto-cyclopentadienyl ring. It was therefore very surprising when the ^1H NMR spectrum was found to show only two singlets of equal intensity. It was postulated that an η^5,η^1 formulation could still be consistent if the iron-carbon sigma bond were continually shifting among all five carbons of the monohapto ring at a rate sufficient to cause averaging of the ^1H NMR spectrum. The term "ring whizzing" has been applied to such a process.

In 1966, Cotton *et al.*[136] reported an X-ray study of the iron complex which confirmed the $(\eta-C_5H_5)Fe(CO)_2-(5-\eta^1-C_5H_5)$ structure. These same authors recorded the ^1H NMR at -80°C. At this temperature the spectrum showed the pattern expected for a $5-\eta^1-C_5H_5$ ring. As the temperature was raised these signals collapsed, then reappeared as a single line confirming the original suggestion[80] that $(\eta-C_5H_5)Fe(CO)_2(5-\eta^1-C_5H_5)$ was fluxional *via* a ring whizzing process.

Many other examples of η^1-cyclopentadienyl complexes of the transition metals have since been shown to exhibit similar fluxional behavior.[137,138] It was long presumed that $7-\eta^1$-cycloheptatrienyl compounds would also be fluxional with metal migration about the C_7H_7 ring. The difficulties encountered in the preparation of $7-\eta^1-C_7H_7$ derivatives of the transition metals prevented such a study until 1979. In that year the first monohaptocycloheptatrienyl complex of a transition metal, $(CO)_5Re(7-\eta^1-C_7H_7)$ was reported by Heinekey and

Graham.[139] The solution structures were investigated with ^1H NMR spectroscopy and the complex shown to be fluxional by a process similar to that of the η^1-C_5H_5 complexes.

The fluxional behavior of transition metal η^1-cyclopolyenyl systems may be similar to the sigmatropic rearrangements of organic chemistry. It has been suggested[140] that the path of metal migration could be expected to obey orbital symmetry rules.[141] To test the validity of these rules as applied to sigmatropic rearrangements[142] with transition metal complexes, it is necessary to determine the pathway by which metal migration occurs. The tool which has been used most frequently in such studies is NMR spectroscopy.

There are two NMR methods which have been used to monitor sigmatropic rearrangements in η^1-cyclopolyenyl complexes. The technique which has received by far the wider application is line shape analysis.[116] This method utilizes the broadening of NMR signals which occurs when the corresponding nuclei are exchanged at rates which are comparable to their separation in chemical shift. The shape of the NMR peaks for nuclei affected by the sigmatropic rearrangement can be correlated to the pathway of migration. An example of the changes in ^1H NMR spectra of 5-η^1-C_5H_5 complexes at various rates of exchange is provided by the variable temperature NMR of $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$ described above.

A second NMR technique which has been used more recently to detect fluxionality involves spin saturation transfer experiments.[143] If a nucleus is saturated by irradiation at its resonance frequency and then moves to a new site at a rate fast compared to its relaxation time, the saturation will also be transferred. The exchange of the nuclei will be reflected in a decrease in intensity at the site to which the irradiated nucleus was transferred. The positions with which the irradiated nucleus exchanges can demonstrate the path of migration. The spin saturation transfer technique was used recently to determine the pathway of fluxionality in $(CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7)$.[139]

The current investigation of the chemistry of the rhenium group has provided an opportunity to prepare monohapto-cycloheptatrienyl and -cyclopentadienyl compounds in the same metal system. The prevalance of fluxional behavior in other η^1-cyclopolyenyl complexes* suggested similar properties might also be exhibited by the rhenium compounds.

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*Fluxional η^1-cyclopolyenyl compounds of the main group elements have also been prepared. For discussions on the chemistry of these complexes see references 116, 140 and 144.

SECTION II

PREPARATION OF η^1-CYCLOPOLYENYL COMPOUNDS OF THE RHENIUM GROUP.

A. Introduction.

The routes used to prepare η^1-cyclopolyenyl complexes of the transition metals have been dictated by the nature of the organic ligand. Cyclopentadiene and cycloheptatriene can be converted to anions and cations respectively, which have the aromatic stabilization of six π-electrons.

$$C_5H_6 \longrightarrow C_5H_5^- \qquad\qquad C_7H_8 \longrightarrow C_7H_7^+$$

These reagents, the first a nucleophile, the second an electrophile, provide convenient starting points for the preparation of cyclopolyenyl compounds.

It appears there are two factors most important in the isolation of a transition metal monohaptocyclopolyenyl compound. The metal group must be able to provide a stable metal-carbon sigma bond with the cyclopolyenyl ligand *and* there can be no facile pathways to species of higher hapticity under the reaction conditions. The influence of these factors is apparent from a comparison of early attempts to prepare η^1-C_5H_5 and η^1-C_7H_7 compounds.

The first reactions which would have been expected to give η^1-C_5H_5 complexes were performed in the early

1950's. It was found that the cyclopentadienyl ion would react with many of the transition metal halides to give stable, isolable complexes. However, these reactions usually generated pentahaptocyclopentadienyl products, presumably through monohapto intermediates. Soon afterwards it was discovered that with coordinately and electronically saturated halides, η^1-C_5H_5 products could be isolated.

The iron iodide, $(\eta$-$C_5H_5)Fe(CO)_2I$, for example, reacts with $C_5H_5^-$ to form $(\eta$-$C_5H_5)Fe(CO)_2(5$-η^1-$C_5H_5)$.[80] The ability of the iron group to maintain an η^1-C_5H_5 ring could be attributed to the nonlability of the carbon monoxide ligands. Consistent with this interpretation, the iron complex is reported[136] to give carbon monoxide and ferrocene on decomposing (i.e., $\eta^1 \rightarrow \eta^5$ conversion). One would expect other metal halides with nonlabile ligands to stabilize monohaptocyclopentadienyl forms with respect to species of higher hapticity.

In reported attempts to prepare η^1-C_7H_7 compounds, problems have been encountered which suggest an inherent low stability of the metal-carbon sigma bond and a tendency to form polyhapto species. In 1958, Wilkinson tried to prepare $(CO)_5Mn(7$-η^1-$C_7H_7)$ from reaction of $(CO)_5Mn^-$ with $C_7H_7^+$.[145] The products of this reaction [Eq (60)] were the corresponding metal dimer and ditropyl.

$$(CO)_5Mn^- + C_7H_7^+ \longrightarrow Mn_2(CO)_{10} + (C_7H_7)_2 \qquad (60)$$

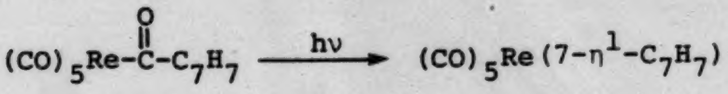
The isolation of these coupled products has been taken as evidence[146] for the instability of η^1-C_7H_7 complexes of the transition metals.

In 1968, a similar reaction of tropylium cation with $(\eta$-$C_5H_5)Fe(CO)_2^-$ was reported[147] to give the trihapto complex, $(\eta$-$C_5H_5)Fe(CO)_2(\eta^3$-$C_7H_7)$. A new route to η^1-C_7H_7 species was attempted in 1971. Whitesides[148] prepared the acyl compound $(CO)_5Mn-\overset{O}{\overset{\|}{C}}-C_7H_7$. Decarbonylation of the manganese complex would be expected to give $(CO)_5Mn(7$-η^1-$C_7H_7)$, instead the product of low temperature photolysis was the pentahapto species, $(CO)_3Mn(\eta^5$-$C_7H_7)$. These preparations were taken as a further indication of the inherent instability of η^1-C_7H_7 complexes.

In fact, the η^3 and η^5 compounds described above were probably the first evidence for the existence of η^1-C_7H_7 species. It seems probable that a monohapto-cycloheptatrienyl metal complex was an intermediate in both the iron and manganese preparations. The failure to isolate η^1-C_7H_7 compounds in these metal systems could be attributed to the lability of the carbonyl ligands under these conditions.

Evidence for this suggestion is provided by the preparation in 1979 of $(CO)_5Re(7$-η^1-$C_7H_7)$.[139] The rhenium compound can be obtained from either of the reactions shown in Eqs (61) and (62). The authors suggest

$$(CO)_5Re^- + C_7H_7^+ \longrightarrow (CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7) \qquad (61)$$



$$(CO)_5Re\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_7H_7 \xrightarrow{h\nu} (CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7) \qquad (62)$$

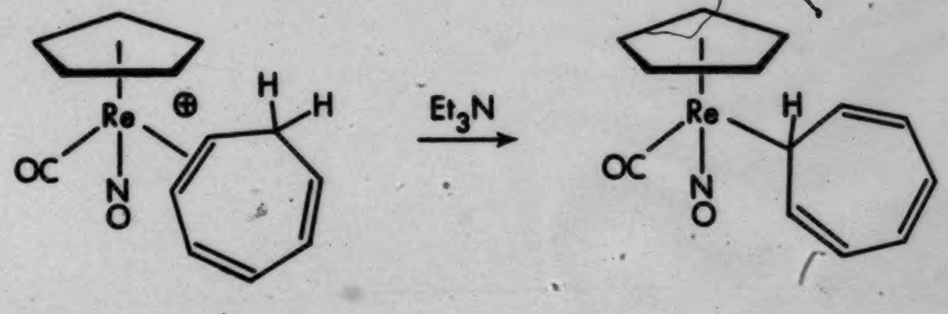
the stability of the rhenium compound is due in part to the strength of the rhenium-carbon sigma bond. The stability of $(CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7)$ with respect to species of higher hapticity could be attributed to the reluctance of the $(CO)_5Re\text{-}$ group to dissociate carbon monoxide. The rhenium compound can be *induced* to eliminate CO giving the trihapto, $(CO)_4Re(\eta^3\text{-}C_7H_7)$ and pentahapto, $(CO)_3Re(\eta^5\text{-}C_7H_7)$ complexes.[149]

The nature of other alkyl derivatives of the rhenium group suggested $\eta^1\text{-}C_5H_5$ and $\eta^1\text{-}C_7H_7$ complexes if they could be formed would be stabilized by a high rhenium-carbon sigma bond strength. The nonlability of the ligands in the CpRe(CO)(NO)- system further suggested such compounds could be maintained at the monohapto- stage. The preparation of η^1-cyclopolyenyl complexes of the rhenium group will be described chronologically, beginning with the cycloheptatrienyl system.

B. Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$.

The methods discussed above for the preparation of $\eta^1\text{-}C_7H_7$ derivatives involved use of the corresponding metal anions. As all attempts to prepare $[(\eta\text{-}C_5H_5)Re(CO)(NO)]^-$ have been unsuccessful an alternate synthetic approach was required. Fortunately an entry to cycloheptatriene chemistry of the rhenium group, $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) was already available from a study of the reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) with organic electrophiles (Chapter III).

The cycloheptatriene cation 18 reacts rapidly with Et_3N in CH_2Cl_2 to give a red solution from which was isolated a dark red crystalline compound (22). Consistent with the color and solubility characteristics of the new compound, infrared monitoring indicated formation of a neutral species of the rhenium group. Mass spectrum and elemental analysis suggested the new compound had the formula $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_7H_7)$ (22). The proton and carbon NMR spectra of 22 (see Section IV) are totally consistent with its formulation as the monohaptocycloheptatrienyl complex, $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ [Eq (63)].



(63)

The η^1-cycloheptatrienyl compound 22 shows excellent air and thermal stability (MP 94-95°C). In solution the complex decomposes slowly at 130°C ($\tau_{1/2} \simeq 76$ min, DMSO-d_6) forming ditropyl and the rhenium dimer, $[(\eta\text{-}C_5H_5)Re(CO)(NO)]_2$. Under these thermal conditions there was no evidence for formation of η^3- or η^5-C_7H_7 products. The possibility of photochemically inducing such a reaction has not yet been investigated. Thermally, 22 is substantially more stable than $(CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7)$ for which the calculated half life at 130°C is 16.3 sec. It would seem that the strength of the rhenium-carbon sigma bonds in these complexes is highly dependent on the nature of the other ligands to which the metal is bonded.

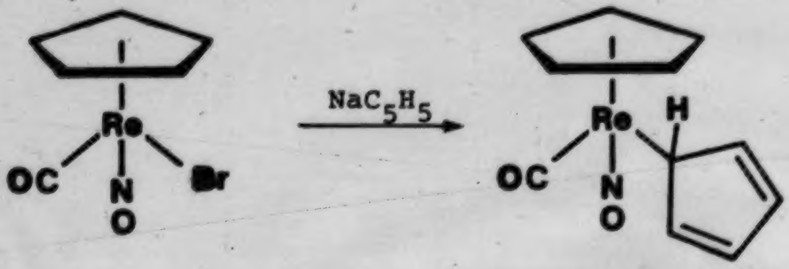
The yield of the reaction shown in Eq (63) was 90%. It was anticipated that this route could be extended to the other metal systems. Given the number of reported transition metal hydrides, if reaction with $C_7H_7^+$ to give cycloheptatriene cations like 18 proves to be a general process it will provide access to many new η^1-C_7H_7 compounds. This would be particularly useful in systems where the corresponding anion is not available. Initial results have been promising; to date this method has been used to prepare $(\eta\text{-}C_5H_5)Os(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)$, $(\eta\text{-}Me_5C_5)Os(CO)_2$-$(7\text{-}\eta^1\text{-}C_7H_7)$,[101] and $(\eta\text{-}Me_5C_5)Ru(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)$.[149]

C. Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$.

Two routes have been found for preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$. The first of the syntheses to be discussed utilizes the reaction of NaCp with a metal halide. The availability of cations of the rhenium group $[(\eta\text{-}C_5H_5)Re(CO)(NO)(L)]^+$ containing labile ligands, L suggested a second method.

The bromo derivative, $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9) provides a convenient starting material for the preparation of an $\eta^1\text{-}C_5H_5$ derivative of the rhenium group. Addition of NaCp to a THF solution of (9) at -15°C resulted in a rapid reaction with some decomposition. Infrared monitoring indicated generation of an alkyl complex of the rhenium group. Solvent removal gave a black residue from which could be isolated a red crystalline compound (23). The mass spectrum and elemental analysis suggested 23 be formulated as $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_5H_5)$, obtained in 42% yield.

The 18-electron rule predicts the second C_5H_5 ring of 23 would be bonded in η^1 fashion; this was confirmed by ^1H and ^{13}C NMR studies (see Section IV). Presumably the monohaptocyclopentadienyl compound is formed by nucleophilic displacement of Br^- from 9 [Eq (64)]. This reaction may occur by direct attack at Re, or by initial formation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(C(O)C_5H_5)]^-$, followed by



(64)

elimination of Br^-. The new complex 23 shows good oxidative and thermal stability.

The monohaptocyclopentadienyl derivative 23 can also be prepared from the cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(THF)]^+$. The THF cation reacts very rapidly with NaCp in THF at -20°C as shown in Eq (65). As discussed in Chapter III,

$$[(\eta\text{-}C_5H_5)Re(CO)(NO)(THF)]^+ \xrightarrow[THF]{NaCp} (\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5) \qquad (65)$$

$[(\eta\text{-}C_5H_5)Re(CO)(NO)(THF)]^+$ may rapidly dissociate THF in solution. The reaction of Eq (65) might therefore occur with prior loss of THF to give coordinatively unsaturated $[(\eta\text{-}C_5H_5)Re(CO)(NO)]^+$ which would readily be attacked by NaCp. As the yield of Eq (65) is 29%, the bromide route is the preferred method for preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$.

The infrared spectrum of $\underset{\sim}{23}$ is shown in Figure VII. In hexane, the compound shows two sharp carbonyl bands at 1989.2(m) and 1971.9(s) cm^{-1}. The terminal nitrosyl region has one somewhat broad band at 1720.2 cm^{-1}, believed due to two unresolved peaks. An identical infrared spectrum was obtained with product prepared from either Eq (64) or Eq (65). Fractional crystallization and sublimation produced no change in the intensities of the infrared bands of $\underset{\sim}{23}$. It is suggested that the two sets of peaks exhibited by $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ are due to the existence of rotamers about the $Re\text{-}(5\text{-}\eta^1\text{-}C_5H_5)$ sigma bond. A similar phenomena has been reported for the iron compound $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$.[150]

There is no evidence for conversion of the $\eta^1\text{-}C_5H_5$ ring of $\underset{\sim}{23}$ to η^3 or η^5 bonding modes. The compound has been heated in toluene to 110°C with no sign of reaction or decomposition. In hexane, ultraviolet irradiation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ gave only a very slow decomposition to unidentified products insoluble in organic solvents.

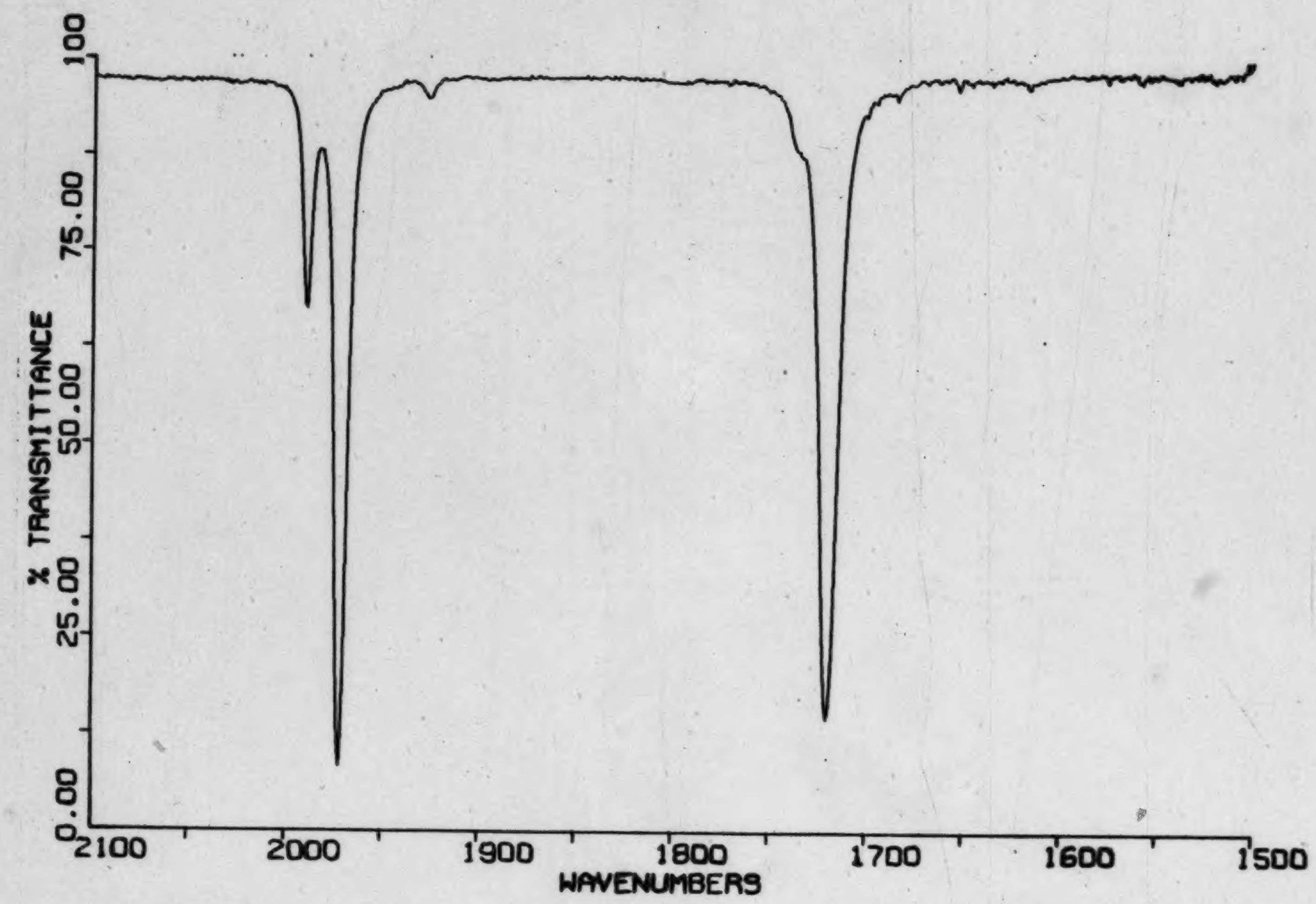


FIGURE VII. Infrared Spectrum of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$, hexane.

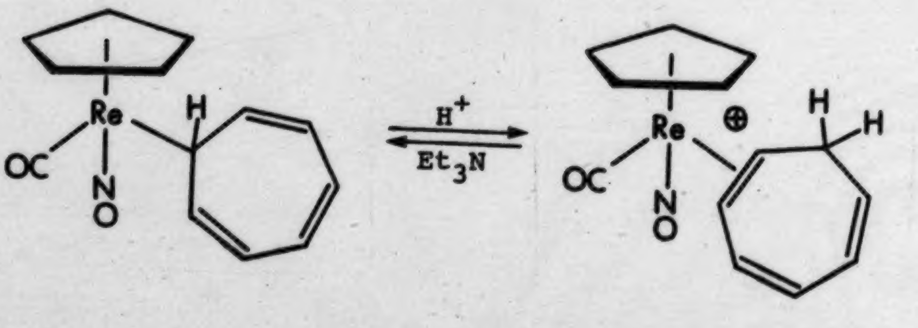
SECTION III

INTERCONVERSTION OF η^1-CYCLOPOLYENYL AND η^2-CYCLOPOLYENE COMPLEXES OF THE RHENIUM GROUP.

The η^1-cyclopolyenyl complexes of the rhenium group are susceptible to attack by electrophiles. These reactions occur with formation of cationic η^2-cyclopolyene derivatives of $(\eta\text{-}C_5H_5)Re(CO)(NO)$-. The reverse reactions $\eta^2 \rightarrow \eta^1$ have also been studied.

A. Reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ and $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ with Electrophiles.

The route used to prepare $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) involved deprotonation of the 1,2-η^2-cycloheptatriene cation 18. Complex 22 can be protonated with strong acids to regenerate the cycloheptatriene cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+$ as shown in Eq (66).



(66)

Dropwise addition of $HBF_4 \cdot Et_2O$ to a diethyl ether solution of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) resulted in an almost instantaneous precipitation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) isolated in 94% yield. The cycloheptatriene cation 18 prepared in this manner is identical to that obtained from reaction of $(\eta\text{-}C_5H_5)Re(CO)(NO)H$ (5) with $C_7H_7^+BF_4^-$ (Chapter III, Section IV). The protonation of 22 has also been carried out with anhydrous HCl and CF_3COOH. With these acids the process is more complex due to a further reaction.

When gaseous HCl was briefly passed through a red CH_2Cl_2 solution of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (23) an immediate reaction occurred resulting in a yellow color. Infrared monitoring indicated formation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+$. Gradually, as the reaction mixture was stirred at room temperature the solution turned red. Infrared spectroscopy then indicated formation of a neutral complex of the rhenium group. Proton NMR of a sample of the reaction mixture showed the presence of cycloheptatriene and an $\eta\text{-}C_5H_5$ signal in a region expected for a halide compound of the rhenium group. The rhenium product was isolated and shown to be the chloride $(\eta\text{-}C_5H_5)Re(CO)(NO)Cl$ (25). The properties of 25 are very similar to those of the bromide $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9).

A similar sequence of reactions occurred on addition of trifluoroacetic acid to a CH_2Cl_2 solution of

$(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$. From this reaction a trifluoroacetate complex of the rhenium group $(\eta\text{-}C_5H_5)$-$Re(CO)(NO)(OC(O)CF_3)$ (26) was isolated as orange crystals (MP = 134-135°C) in 81% yield. The thermal and oxidative stability of 26 is similar to that of other neutral $(\eta\text{-}C_5H_5)Re(CO)(NO)$- derivatives. The solubility and spectral parameters of 26 are intermediate between those of the halides and the cations of the rhenium group. The infrared spectrum of $(\eta\text{-}C_5H_5)Re(CO)(NO)(OC(O)CF_3)$ (26) shows a somewhat broad peak at 1716(m) cm^{-1}, assigned to the acetate carbonyl stretching mode. The metal carbonyl and nitrosyl regions show two sets of bands similar to those found for the monohaptocyclopentadienyl complex 23; this is attributed to rotamers about the rhenium-oxygen bond.

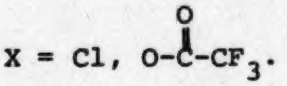
Trifluoroacetate complexes of the transition metals were reported by Wilkinson, *et al.* in 1962.[86] The compounds $(\eta\text{-}C_5H_5)M(CO)_3(OC(O)CF_3)$, M = Mo, W were obtained on protonation of the corresponding hydrides with $CF_3COOH\text{-}BF_3\text{-}H_2O$. The authors provided evidence to show that these reactions occurred with initial formation of $[(\eta\text{-}C_5H_5)M(CO)_3(H)_2]^+OC(O)CF_3^-$, followed by reductive elimination of hydrogen.* Presumably a similar process occurs on protonation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22)

---

*Similar reactions with $(\eta\text{-}C_5H_5)M(CO)_3CH_3$ (M=Mo,W) generated the trifluoroacetate complexes and methane.

with HCl and CF_3COOH. As suggested by the reaction of 22 with HBF_4, initial protonation would give olefin cations of the type $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+X^-$, X = Cl, $O\text{-}C(O)CF_3$. A slower second reaction must then occur in which the counter ions displace cycloheptatriene to give the isolated products [Eq (67)]. Although the

$$
\begin{aligned}
&(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7) \xrightarrow{HX} \\
&\qquad [(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]^+X^- \longrightarrow \qquad (67) \\
&\qquad (\eta\text{-}C_5H_5)Re(CO)(NO)X + C_7H_8
\end{aligned}
$$



$X = Cl,\ O\text{-}\overset{\overset{\textstyle O}{\|}}{C}\text{-}CF_3.$

cycloheptatriene ligand can apparently be displaced by the anionic nucleophiles Cl^- and $CF_3CO_2{}^-$, reaction of 18 with triphenylphosphine at room temperature gave no evidence for $[(\eta\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]^+$ (14).

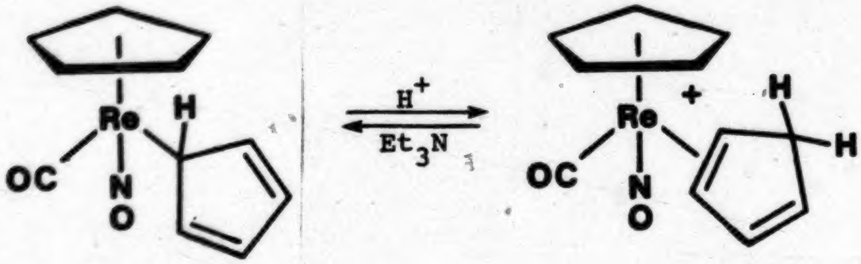
Reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) with electrophiles other than H^+ have also been explored. Initial results indicate that 22 is susceptible to attack by a variety of alkyl cations, such as Ph_3C^+, $C_7H_7{}^+$, Me_3O^+ and Et_3O^+. These reactions occur to give substituted cycloheptatriene cations of the rhenium group [Eq (68)]. The cationic products can be deprotonated with Et_3N to give substituted $\eta^1\text{-}C_7H_6R$ compounds. This method can be used to prepare a number of new substituted

$$(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7) \xrightarrow{R^+}$$
$$[(\eta\text{-}C_5H_5)Re(CO)(NO)(C_7H_7R)]^+ \xrightarrow{Et_3N} \quad (68)$$
$$(\eta\text{-}C_5H_5)Re(CO)(NO)(C_7H_6R)$$

monohaptocycloheptatrienyl complexes but this was not pursued.

* * * * *

The monohaptocyclopentadienyl compound 23 can be protonated in a reaction similar to that of $(\eta\text{-}C_5H_5)$-$Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22). When HBF_4 etherate was added to a red Et_2O solution of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ (23) a rapid reaction occurred to give a yellow precipitate. The color and solubility of the new compound suggested a cation of the rhenium group. The infrared spectrum of the precipitate was very similar to that of the cycloheptatriene complex 18. Elemental analysis suggested the product be formulated as $[(\eta\text{-}C_5H_5)Re(CO)(NO)(C_5H_6)]BF_4$ (27). The ^1H NMR of 27 (see Section III-C) is consistent with coordination of the rhenium group to one double bond of cyclopentadiene to give a $1,2\text{-}\eta^2$ olefin complex [Eq (69)]. The protonation of 23 is readily reversible; treatment of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]^+$ with Et_3N regenerates the monohaptocyclopentadienyl complex 23 [Eq (69)]. Both these reactions occur in greater than



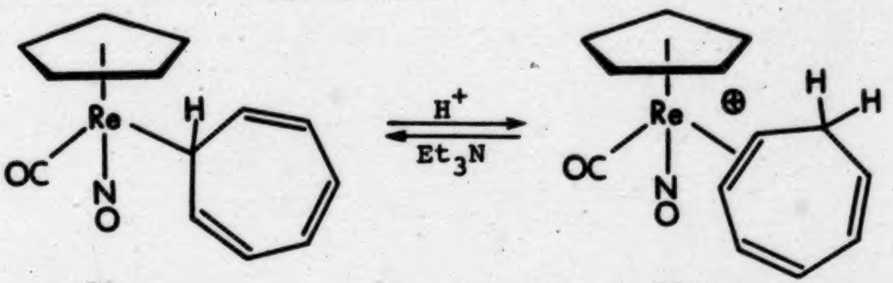
(69)

90% yield.

Protonation of an η^1-cyclopentadienyl transition metal complex has been reported previously. In 1962, Green[151] reacted $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$ with dry HCl in Et_2O. Replacement of the chloride counter ion with PF_6^- gave a stable product formulated as $[(\eta\text{-}C_5H_5)Fe(CO)_2(1,2\text{-}\eta^2\text{-}C_5H_6)]PF_6$. The structure of the iron compound was suggested by proton NMR spectroscopy.

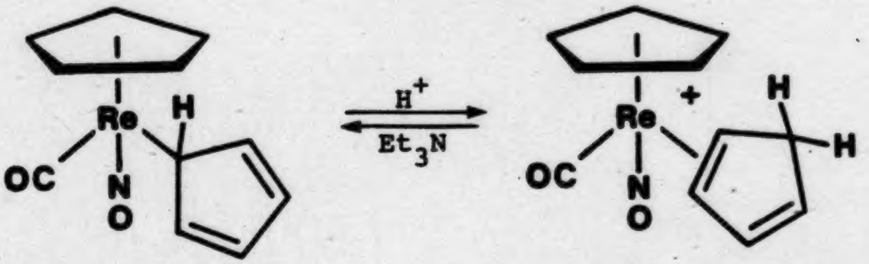
* * * * *

The interconversion of η^1-cyclopolyenyl and η^2-cyclopolyene complexes of the rhenium group [Eqs (66) and (69)] present interesting examples of the behavior modification which can occur on coordination of an organic molecule or functional group to a transition metal.



(66)

22 18



(69)

23 27

The protonation reactions are presumably similar to the conversion to η^1-allyl to η^2-propene complexes. Such reactions have been studied[134] for a number of sigma allyl compounds of iron. It was shown that H^+ attack on $(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}C_3H_2\text{-}C_2H{=}C_1H_2$ occurred at C_1 to give $[(\eta\text{-}C_5H_5)(CO)_2Fe(2,3\text{-}\eta^2\text{-}C_3H_6)]^+$. These results would suggest protonation of 22 and 23 occurs at C_2, followed by rearrangement to give the olefin cations. The *initial* site of H^+ attack might be at rhenium to form a hydridoalkyl cation followed by transfer of H^+ to the organic ring. Wilkinson's results on protonation of $(\eta\text{-}C_5H_5)M(CO)_3R$ (M = Mo, W; R = H, CH_3) suggest this would be the path when the alkyl group is saturated.

In the reverse reactions of Eq (66) and (69); cyclopentadiene and cycloheptatriene have been deprotonated with the weak base Et_3N.* Coordination of the olefin ring to the positive metal center would be expected to increase the acidity of the methylene protons. This postulate and the inherent acidity of cyclopentadiene provide a rationale for the deprotonation of 27 wili Et_3N. Reaction of the cycloheptatriene cation with Et_3N is a much more surprising result.

Cycloheptatriene is a very weak acid with an estimated pK_a of 36.[153] Deprotonation of 18 with Et_3N indicates that coordination to the rhenium group has lowered the pK_a of cycloheptatriene to <3.4 (i.e., pK_a for Et_3NH^+). Activation of the cycloheptatriene ligand to this extent suggests deprotonation of 18 may not occur directly from the aliphatic carbon. The forward reaction of Eq (66), protonation of 22 to give 18 may proceed with initial attack of H^+ at the metal. If this is the mechanism of this reaction deprotonation of (18) would occur with initial formation of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)(H)^+]$. Proton loss from such a hydrido-alkyl cation to Et_3N would seem much more reasonable than deprotonation of an sp^3 carbon-hydrogen bond.

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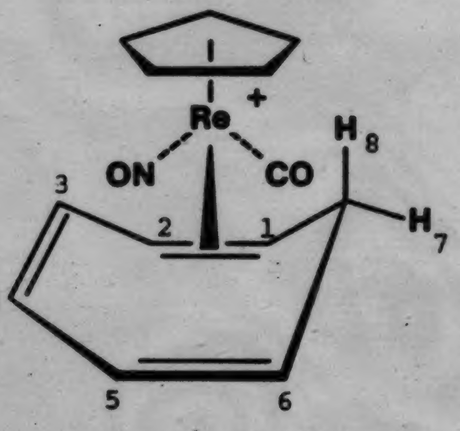
*Deprotonation of olefins coordinated to metal cations has ample precedent,[152] although it is not a general reaction.

B. The Proton NMR Spectra of $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ and $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$.

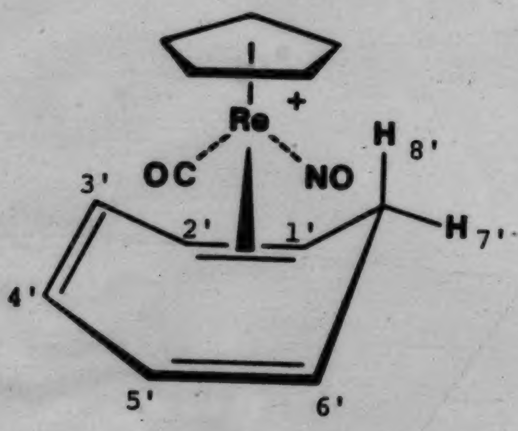
In this section, possible structures for the cyclopentadiene cation $(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) and cyclopentadiene cation $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$ (27) will be discussed. Information on the structures of these olefin complexes has been obtained from infrared and ^1H NMR spectroscopy. Because of the asymmetric metal center, the NMR spectra of these compounds are more complex than might initially be expected. The somewhat simpler cycloheptatriene system will be discussed first.

It appears that only two η^2-cycloheptatriene complexes of the transition metals have been reported in the literature. In 1977 Knox and co-workers[154] prepared $(\eta\text{-}C_5H_5)Mn(CO)_2(1,2\text{-}\eta^2\text{-}C_7H_8)$ from reaction of cycloheptatriene with $(\eta\text{-}C_5H_5)Mn(CO)_2THF$. Reger[155] in 1979 found reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2BF_4$ with C_7H_8 afforded the olefin cation $(\eta\text{-}C_5H_5)Fe(CO)_2(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$. The structures of these complexes were suggested by ^{1}H and ^{13}C NMR spectroscopy (^{13}C only for the iron compound). However, an assignment of the NMR spectra was not given. It has been suggested[155] that coordination of a metal to C_7H_8 occurs at the 1,2 position because this arrangement provides for less ring strain.

Coordination of the rhenium group to cycloheptatriene in 18 also occurs at the 1,2-double bond. As discussed in Chapter I, olefin complexes of $(\eta\text{-}C_5H_5)Re(CO)(NO)$- are expected to show optical isomers. Upon coordination of $(\eta\text{-}C_5H_5)Re(CO)(NO)$- to an olefin with different substituents in cis positions, such as the 1,2 double bond in cycloheptatriene, two diastereomers are formed. The structures of the diastereomers of $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) are shown as 18a and 18b.*



18a



18b

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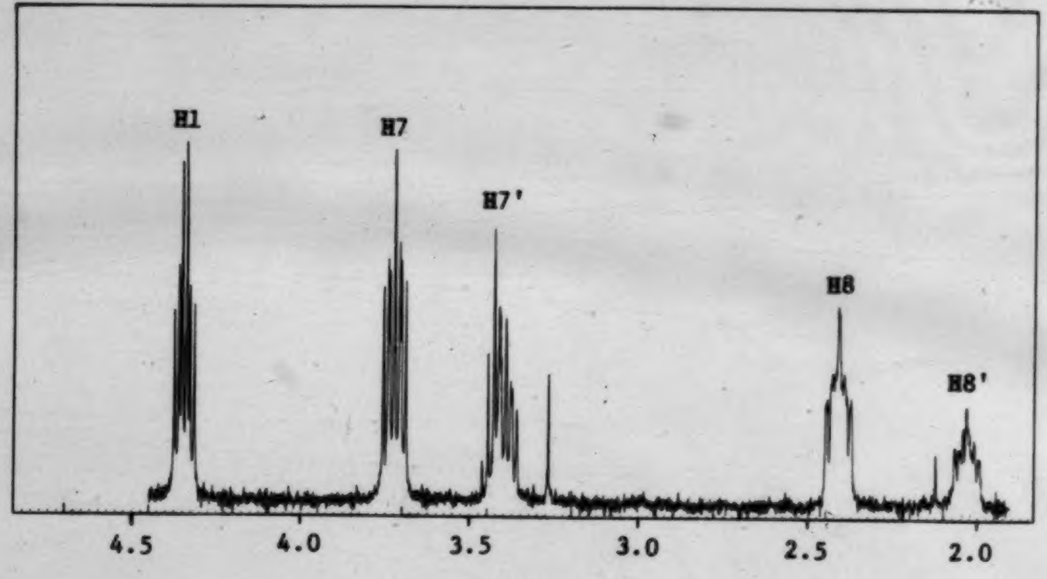
[*] Only one enantiomer of each diastereomer is shown.

Diastereomers of 18 would be expected to show different infrared and NMR spectra.

The 400 MHz, ^{1}H NMR spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ (18) is shown in Figure VIII. The proton NMR of 18 shows two $\eta\text{-}C_5H_5$ singlets at 6.295 and 6.254 ppm of relative intensity 2:1 and two sets of multiplets for the C_7H_8 rings in the same intensity ratio. The numbering scheme used to label the spectrum is shown in 18a and 18b. These labels are provided only for convenience when discussing the spectra, and *no* suggestion of absolute configuration is implied. The assignment of individual peaks in Figure VIII is based on relative chemical shifts, decoupling experiments and on the similarity (in terms of symmetry and multiplicity) of corresponding multiplets in the two diastereomers. The multiplets due to corresponding hydrogens on the two diastereomers have very similar coupling patterns. This is particularly noticeable for the proton pairs H_7, H_7'; H_8, H_8'; H_1, H_1'; H_2, H_2'; and H_3, H_3'. Allowing for the presence of diastereomers the ^{1}H NMR of 18 is similar to that reported for $(\eta\text{-}C_5H_5)Mn(CO)_2(1,2\text{-}\eta^2\text{-}C_7H_8)$.[154]

The spectrum shown in Figure VIII can be divided into three regions. At high field, between 2.0 and 4.0 ppm, there are four signals assigned to the aliphatic protons H_7, H_8 and the corresponding positions, H_7', H_8'



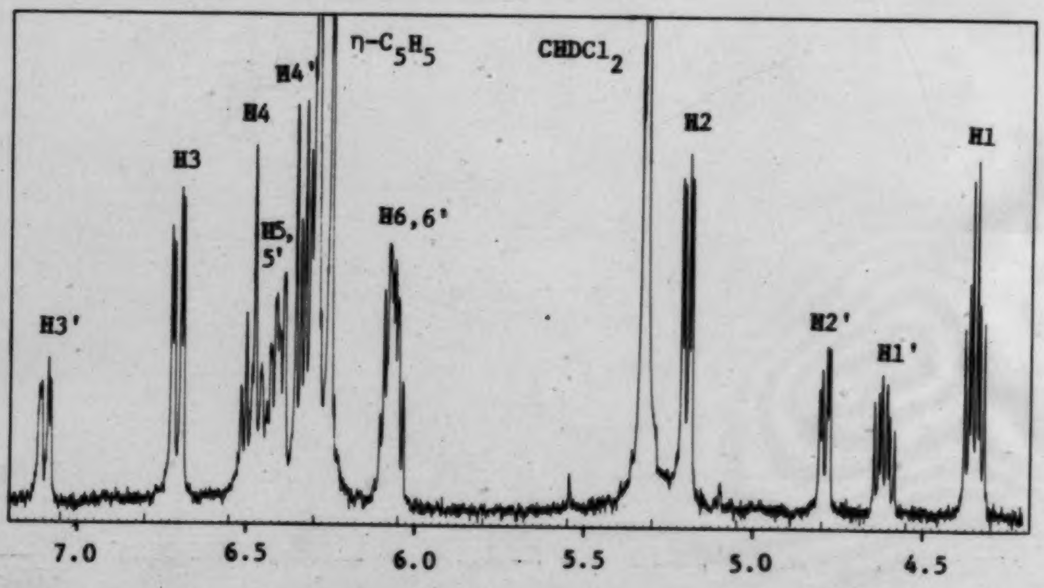


FIGURE VIII. ^{1}H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$, 400 MHz, CD_2Cl_2. The peak assigned to H1 has been reproduced in both expansions.

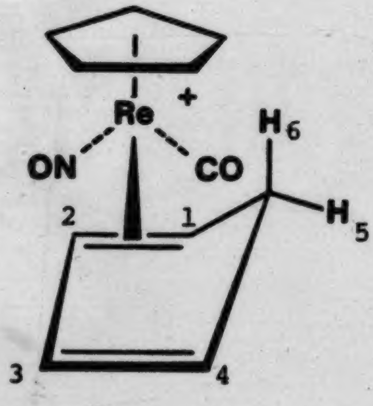
of the minor diastereomer $J(H_7-H_8) \simeq J(H_7'-H_8') = 13.8$ Hz. The two multiplets at 2.05 and 2.42 ppm were assigned to H_8, H_8' on the assumption that close proximity to rhenium would shift these protons to higher field than H_7, H_7'.

Peaks in the region between 4.0 and 5.5 ppm are attributed to protons of the 1,2 double bond. Coordination to the metal center would be expected to shift the resonances of these protons to higher fields[156] than those of the uncoordinated 3,4 and 5,6 double bonds. Irradiation of the aliphatic positions resulted in loss of large couplings to the multiplets at 4.36 and 4.65 ppm. These signals are therefore assigned to H_1, H_1', the protons closer to the aliphatic carbon.

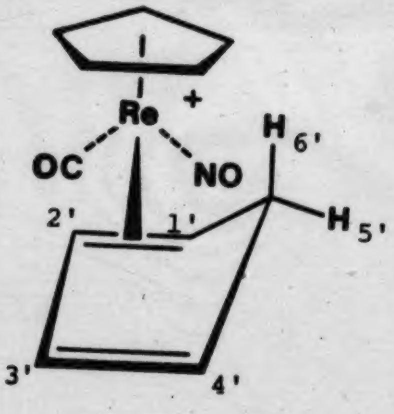
The region from 6.0 to 7.2 ppm contains signals for protons on the uncoordinated double bonds. Assignments in this region are more difficult as some of the signals for corresponding protons on the two diastereomers overlap. Decoupling experiments provided the basis for deciding which portions of these multiplets were due to each diastereomer.

In the structures of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$ shown in 18a and 18b the metal occupies a position *above* the bent C_7H_8 ring. The rhenium group could be bonded to the opposite side of the 1,2 double bond but examination of molecular models suggests that arrangement would be less favored sterically. In uncoordinated cycloheptatriene the ring undergoes a rapid inversion between the two boat conformations. Upon coordination to the rhenium group this motion may be restricted. As expected, the proton NMR of Figure VIII shows the difference in chemical shifts between corresponding protons on the two diastereomers is greatest for those positions closest to the asymmetric metal center.

The 400 MHz, ^{1}H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]\text{-}BF_4$ (27) is shown in Figure IX. Coordination of the rhenium group to one double bond of the cyclopentadiene ring would give rise to the two diastereomers pictured as 27a and 27b.* The proton NMR of 27 shows $\eta\text{-}C_5H_5$ signals



27a



27b

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[*] Only one enantiomer of each diastereomer is shown.

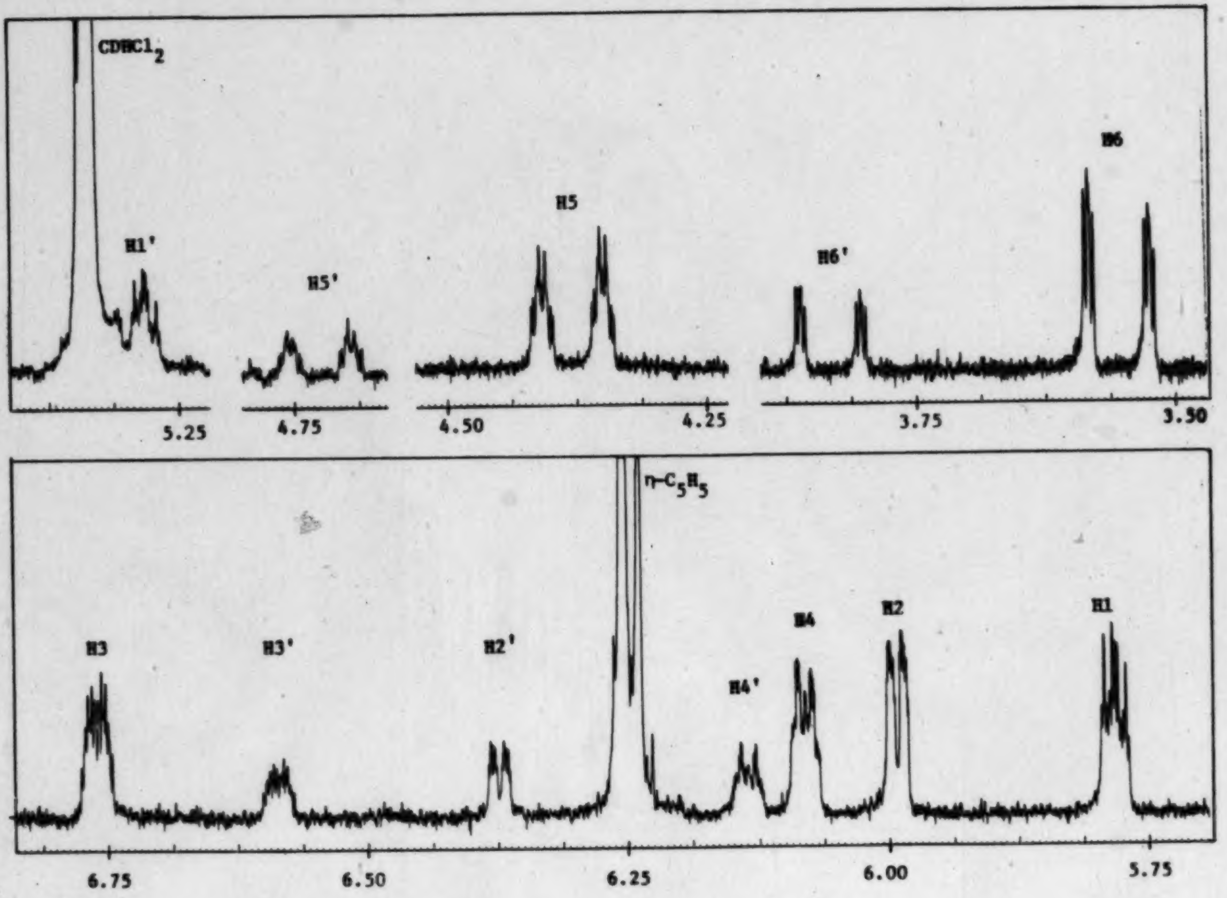

FIGURE IX. ^{1}H NMR of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$, 400 MHz, CD_2Cl_2.

assigned to the two diastereomers at 6.250 and 6.230 ppm in a 3:1 ratio. Assignment of the remainder of the spectrum is based on relative chemical shifts, peak intensities, decoupling experiments and comparison to the proton NMR of the cycloheptatriene cation 18.

The size of the coupling constants in the cyclopentadiene system is on average much smaller than those of the cycloheptatriene cation 18. The only large coupling is between the methylene protons H_5 (H_5') and H_6 (H_6') $J(H_5-H_6) \simeq J(H_5'-H_6') = 23.3$ Hz. As a result the assignment of the ^1H NMR of 27 is made with less confidence than that of the 1,2-η^2-C_7H_8 analog. The chemical shift difference between corresponding protons as assigned in Figure IX is consistent with the proximity of the protons to the asymmetric metal center.

Arguments for the assignments are based upon visual comparison of many spectra with and without decoupling. The conclusions which are somewhat tentative in several cases, are often based upon qualitative changes in a complex multiplet, which are not readily verbalized. On the other hand, it would not be possible to reproduce all the relevant spectra in a thesis of reasonable length. Since the details of the assignments of the η^2-C_5H_6 cation 27 constitute a minor aspect of the work, the decision was made to state only the tentative assignments without presenting the detailed arguments that support them.

* * * * *

The presence of diastereomers for the olefin complexes 18 and 27 should in principle also be detectable by infrared spectroscopy. The relevant spectra are shown in Figures X and XI. In CH_2Cl_2 the cycloheptatriene cation 18 has bands at 2051 (br,s) and 1777.5 (s) cm^{-1} assigned to ν(CO) and ν(NO), respectively. The corresponding infrared peaks of 27 were found at 2053(br,s) and 1779.5(s) cm^{-1}. Somewhat surprisingly the only evidence for diastereomers is the slight asymmetry of the carbonyl bands. The shape of these peaks may be caused by the presence of two overlapping bands due to the two diastereomers.* The difference in the diastereomers is not evident at all in the nitrosyl bands.

The infrared frequencies of the olefin complex 18 and 27 are higher than any of the other cations of the rhenium group prepared in this study. This observation is consistent with the π-acceptor properties of the olefinic ligands.

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*The asymmetry of the carbonyl bands of 18 and 27 are more obvious when the spectra are expanded. Much of this effect is lost in the reductions shown in Figures X and XI.

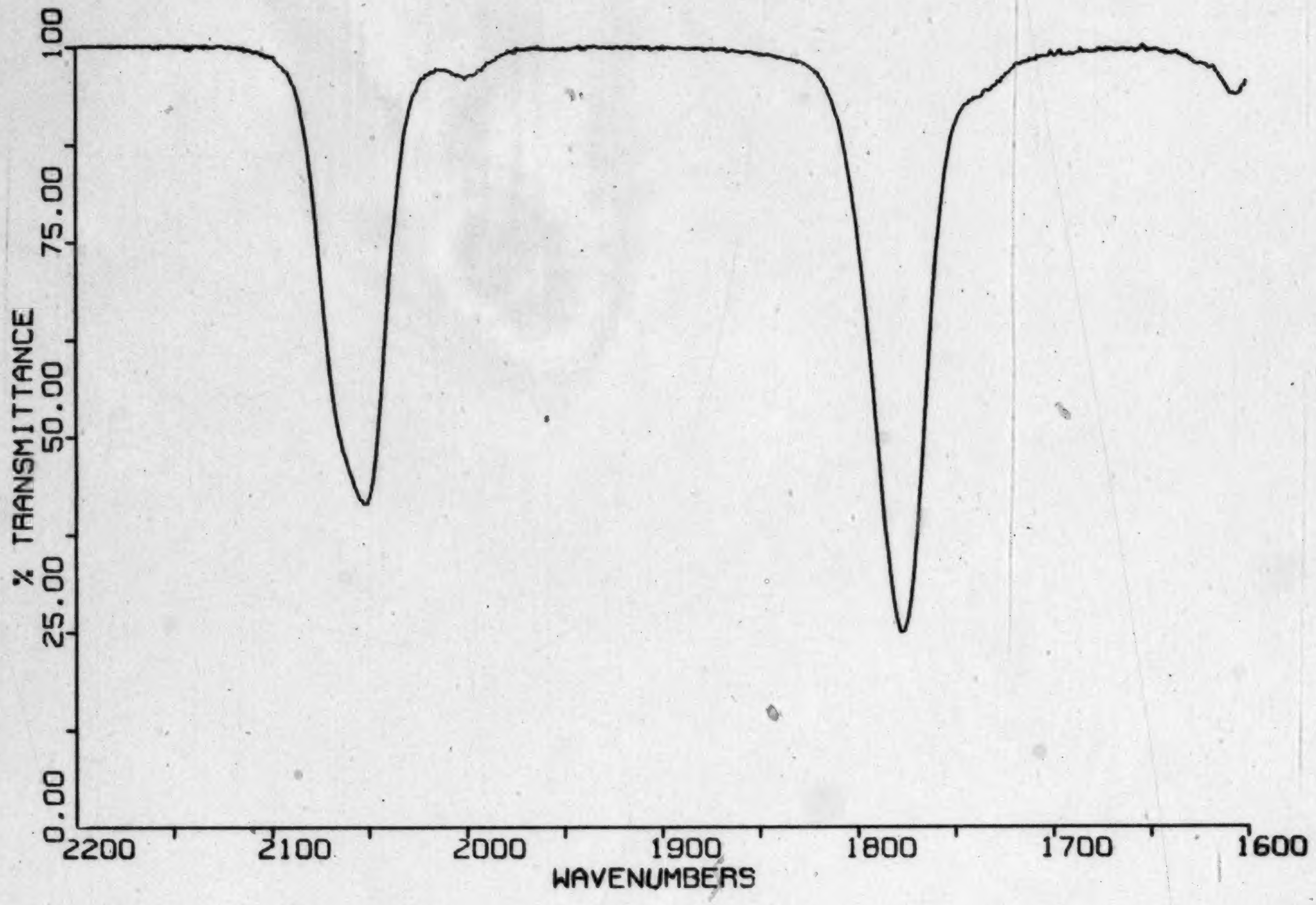


FIGURE X. Infrared Spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_8)]BF_4$, CH_2Cl_2.

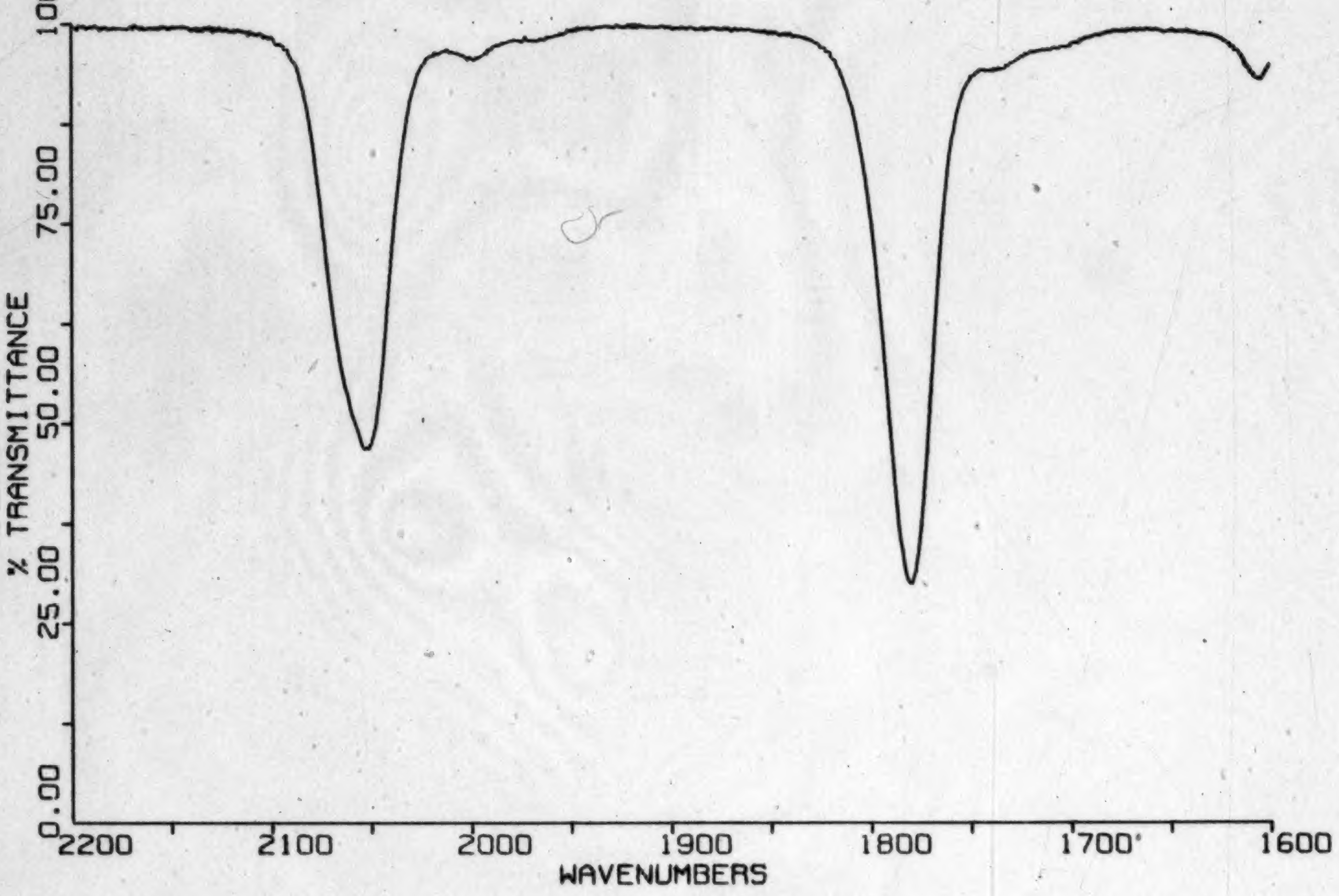


FIGURE XI. Infrared Spectrum of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$, CH_2Cl_2.

The structures which have been suggested for the olefin cations **18** and **27** assume little perturbation of the organic ring on coordination to the rhenium group. This may well be an oversimplification of the true structures. No attempt has been made to extract information on the exact conformations of the C_7H_8 and C_5H_6 rings from the ^1H NMR spectra. Diastereomers of these complexes could presumably be separated and their solid state structures determined from an X-ray study.

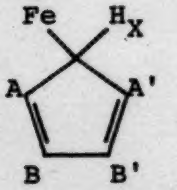
SECTION IV

NMR STUDIES ON η^1-CYCLOPOLYENYL COMPOUNDS OF THE RHENIUM GROUP.

A. Introduction.

As discussed in Section I, transition metal η^1-cyclopolyenyl complexes often show fluxional behavior. These compounds undergo ring whizzing processes *via* sigmatropic shifts of the metal center about the polyenyl ring. NMR spectroscopy has been used in an attempt to observe similar behavior for $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ and $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ and to determine the pathway of any metal migrations.

The first system in which the pathway of sigmatropic rearrangement was established was the monohaptocyclopentadienyl complex $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$.[136] The path of metal migration was determined from a qualitative line shape analysis of the ^1H NMR spectrum. At -89°C, the $\eta^1\text{-}C_5H_5$ portion of this spectrum shows an AA'BB'X pattern at 6.3(m, 2H), 6.0(m, 2H) and 3.5(s,br, 1H) ppm. The



broad peak at 3.5δ can be unambiguously assigned to H_X. The multiplets must be due to the olefinic protons AA'BB'. Assignment of these peaks could not be made from chemical shift arguments or by decoupling experiments.

As the temperature is increased the low field multiplet of the AA'BB' signals broadened at a rate faster than the high field multiplet. This result eliminates the possibility of random shifts by the metal center. It can be shown[116,136] that these line shape changes correspond to a 1,2 (equivalent to 1,5) shift if the low field multiplet at 6.3δ is assigned to the AA' protons or to a 1,3 (1,4) shift if the low field multiplet is due to the BB' protons. Correct assignment of the olefinic region is crucial to the proper choice of the migration pathway.

Cotton, *et al.*[136] assigned the low field multiplet to the AA' hydrogens, those closest to the metal. This decision was initially based on the postulate that the AA' signal would be the more highly coupled of the two olefinic peaks. Confirmation of this assignment was later reported[150] from a computer simulation of the ^1H NMR of the analogous ruthenium complex, $(\eta\text{-}C_5H_5)Ru(CO)_2\text{-}(5\text{-}\eta^1\text{-}C_5H_5)$.* The metal migration was therefore presumed to occur by a series of 1,2 shifts. A number of other

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*There are a number of other arguments which provide evidence for this assignment. See reference 116.

η^1-cyclopentadienyl compounds of the transition metals have been studied and in each case the pathway for fluxionality is believed to involve 1,2 shifts.[137,116,157]

As noted earlier, only one η^1-cycloheptatrienyl complex of a transition metal has been reported.[139] The compound $(CO)_5Re(7-\eta^1-C_7H_7)$ was studied using the spin saturation transfer method (^1H NMR) and shown to be fluxional by a series of 1,2 (1,7) shifts of the metal center about the C_7H_7 ring.

The Woodward-Hoffman symmetry rules for sigmatropic shifts, if they are applicable to η^1-cyclopolyenyl compounds of the transition metals, can be used to suggest the paths of migration which would be symmetry allowed. For η^1-*cyclopentadienyl* compounds these rules predict[142,157] 1,2 shifts are allowed if they occur with *retention* of configuration at the metal; 1,3 shifts are allowed with *inversion* of the metal center. For η^1-*cycloheptatrienyl* complexes the symmetry rules predict[142,157] 1,2 and 1,3 shifts are allowed with *inversion* and 1,4 shifts with *retention* of the metals' configuration. η^1-Cyclopolyenyl compounds of the type discussed above, containing symmetric metal centers, can be used to determine the pathway of sigmatropic shifts but not the stereochemistry.

With a compound in which an η^1-cyclopolyenyl ligand is bonded to an asymmetric metal center it should be possible to determine both the pathway and stereochemistry of the metal migration. Such a complex would be expected to show separate signals for each of the ring protons (or carbons). Analysis of this situation in the course of this work has shown that in principle, a spin saturation transfer experiment could be used to unambiguously establish the stereochemistry of sigmatropic shifts.

The preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) and $(\eta\text{-}C_5H_5)Re(CO)(5\text{-}\eta^1\text{-}C_5H_5)$ (23) provided an opportunity to perform the experiments described above. The 1,2 shifts reported for other transition metal $\eta^1\text{-}C_5H_5$ complexes could be consistent with the predictions of the symmetry rules of a similar process in the rhenium compound 23 were shown to occur with retention. The observation of 1,2 shifts in $(CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7)$[139] suggested any sigmatropic shifts in 22 might occur with inversion of configuration at rhenium if the symmetry rules are applicable to these systems.

B. $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$.

The 400 MHz, ^1H NMR of the η^1-cycloheptatrienyl complex $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (22) is shown in Figure XII. This spectrum was obtained at room temperature. As a result of the asymmetric metal center, separate signals are observed for the seven distinct protons of the C_7H_7 ligand. The assignment shown in Figure XII was determined by decoupling experiments.

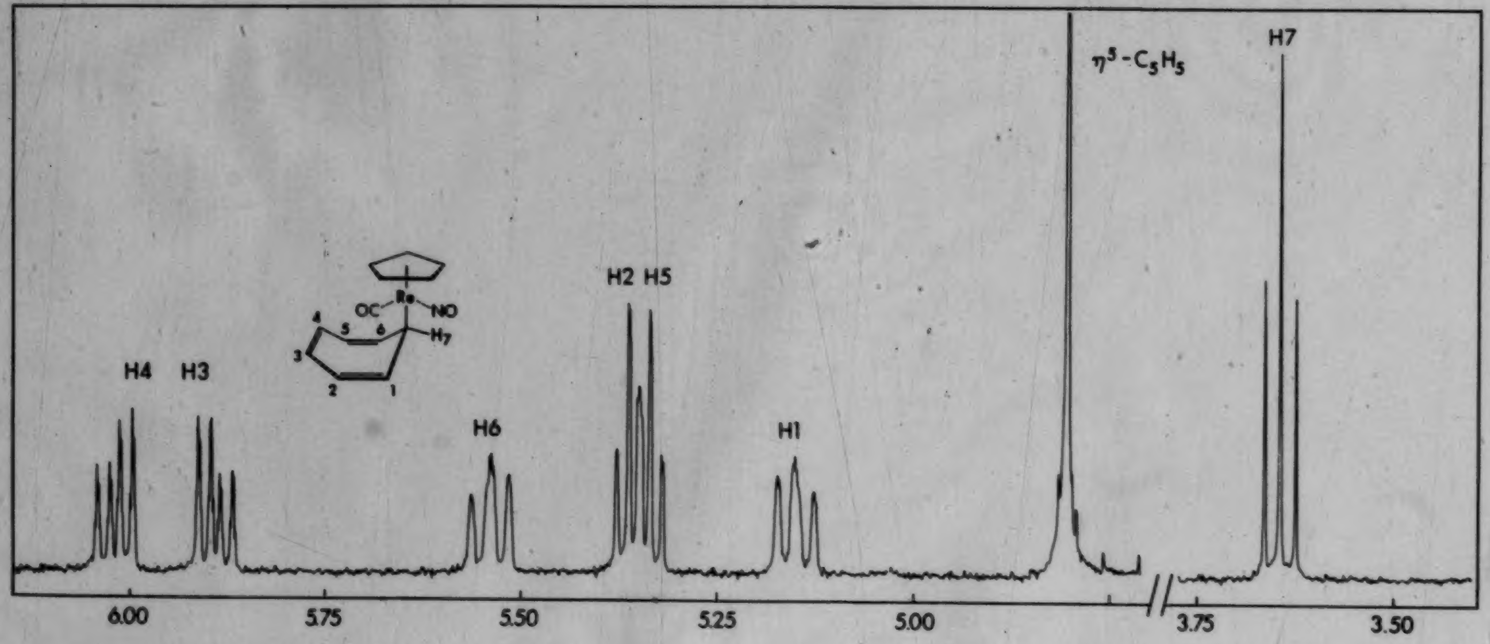
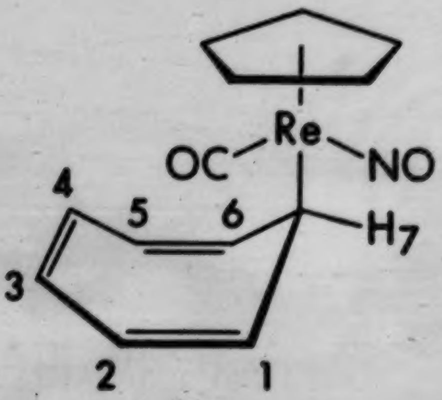


FIGURE XII. ^{1}H NMR of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$, 200 MHz, CD_2Cl_2.

The triplet at 3.65 ppm is assigned to the aliphatic proton H7. The size of the coupling of H7 to H1 and H6 [J(H1-H7) ≃ J(H6-H7) = 8.0 Hz] suggests[139] the rhenium group occupies a quasi-axial position as shown in structure **22a**.* This conformation is consistent with the chemical shift differences between diastereotopic proton pairs (/δH1-δH6/>/δH3-δH4/>/δH2-δH5/). Presumably the closer the protons are to the chiral center the more they will sense the difference in their environments. A similar trend was observed in the ^{13}C NMR of $(\eta$-$C_5H_5)Re(CO)(NO)$-$(7$-η^1-$C_7H_7)$. In benzene-d_6 at 25°C the carbon NMR shows signals at 13.3 (C_7); 91.7 (η-C_5H_5); 122.2 , 122.6 ($C_{2,5}$); 132.8 ; 134.3 ($C_{1,6}$); 139.5 , 140.5 ($C_{3,4}$); 210.2 (CO) ppm. The ^{13}C NMR was assigned by selective proton decoupling.



22a

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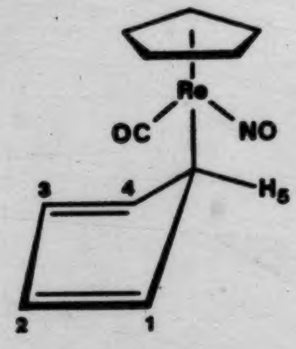
[*] In the solid state, $(CO)_5Re(7$-η^1-$C_7H_7)$ adopts a conformation similar to that shown for **22a**.[149]

The appearance of separate signals for all seven positions of the cycloheptatrienyl ring suggested it would be possible to determine the pathway and stereochemistry of metal migration should the compound be fluxional. Attempts were made to observe sigmatropic shifts by heating $\underset{\sim}{22}$ to +130°C in DMSO-d_6. At this temperature the 200 MHz, ^{1}H NMR remained unchanged from the spectrum obtained at room temperature. A spin saturation transfer experiment at 130°C in DMSO-d_6 showed no evidence for fluxional behavior. This observation implies not only a lack of fluxionality but also that the chiral metal center is configurationally stable at 130°C on the NMR time scale.

The only other reported η^1-C_7H_7 complex of a transition metal, $(CO)_5Re(7\text{-}\eta^1\text{-}C_7H_7)$ exhibited fluxional character observable by ^{1}H NMR in the 15°-40°C range.[139] The barrier to metal migration in $\underset{\sim}{22}$ must be considerably higher than that of the pentacarbonyl compound. Although both compounds decompose to ditropyl and the corresponding metal dimers, the thermal stability of the $(CO)_5Re$- compound is much less than that of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$. The factors which are responsible for the relative Re-C_7H_7 sigma bond strengths in these complexes may also influence their widely different barriers to sigmatropic shifts.

C. $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$.

A reasonable structure for the cyclopentadienyl complex $(\eta\text{-}C_5H_5)Re(CO)(NO)(C_5H_5)$ would contain one η-Cp ring and one η^1-Cp ring as shown in 23. A similar



23

structure has been reported for the iron analog, $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$.[136] Such a formulation is in accord with the ^{13}C NMR of 23. In CH_2Cl_2 at -80°C the carbon NMR spectrum has peaks at 22.1 (C_5); 92.9 ($\eta\text{-}C_5H_5$); 119.6, 120.9 ($C_{2,3}$); 143.9, 145.5 ($C_{1,4}$); and 209.4 (CO) ppm. Assignment of the ^{13}C NMR of 22 is based on the relative chemical shifts and by analogy to that reported[158] for $(\eta\text{-}C_5H_5)Fe(CO)_2(5\text{-}\eta^1\text{-}C_5H_5)$. Consistent with this assignment the size of the chemical shift difference between the diastereotopic carbons C1,4 is greater than that for C2,3.

The proton NMR spectrum of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ *at -80°C* is shown in Figure XIIIa (200 MHz, CD_2Cl_2). The spectrum shows a sharp singlet at 5.46 (5H) ppm and five

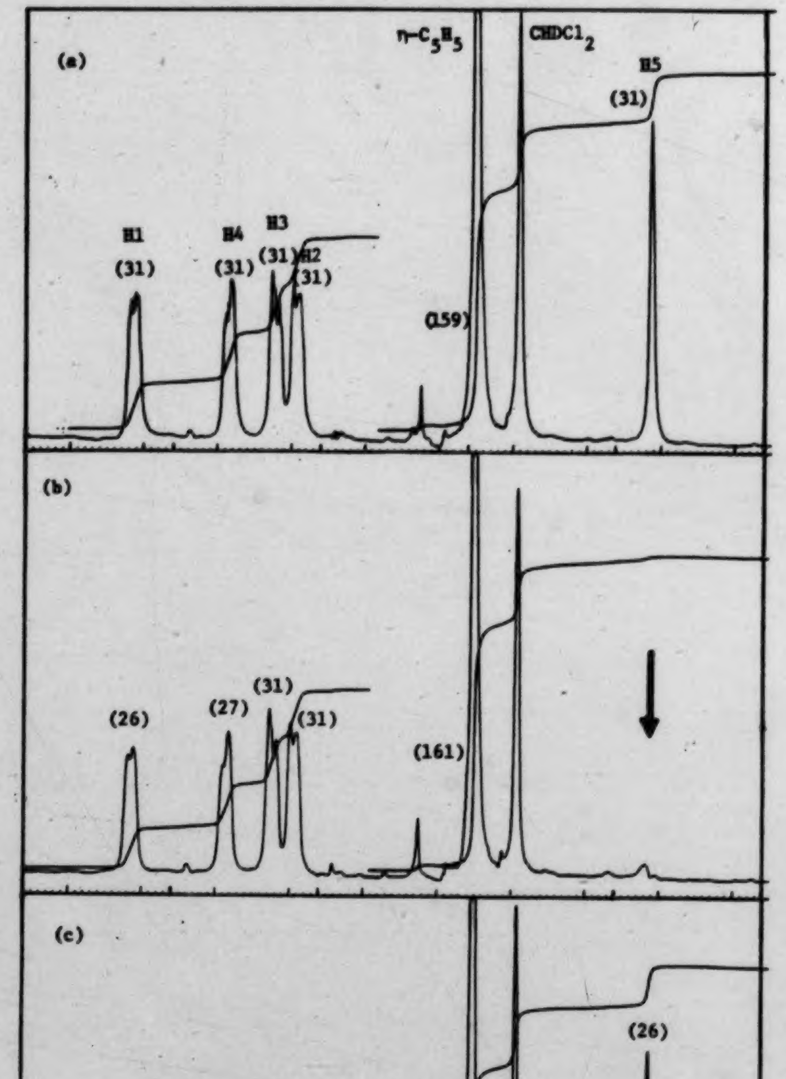


FIGURE XIII. Spin saturation transfer experiments with (η-C_5H_5)Re(CO)(NO)(5-η^1-C_5H_5), CD_2Cl_2, -80°C. Peak intensities are indicated by the numbers in parentheses. The position of saturation is indicated by an arrow (see text).

multiplets each of intensity 1H. On further cooling the spectrum remained unchanged and therefore likely represents the low temperature limit. On warming, the four small multiplets and the signal at 4.90 ppm coalesced and at room temperature formed a broad peak at *ca.* 6.1 ppm. At higher temperatures the peak at 6.1 ppm sharpened to give a singlet of equal intensity to the peak at 5.46 ppm. These observations show $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ is fluxional *via* metal migration about the monohapto ring.

The assignment of the low temperature spectrum of 23 is shown in Figure XIIIa. The singlet at 5.46 ppm is due to the $\eta\text{-}C_5H_5$ ring. On the basis of its chemical shift the peak at 4.90 ppm is assigned to H5, the aliphatic proton. Decoupling of H5 gave only small changes in the four olefinic signals. This, in contrast to the cycloheptatrienyl system makes assignment of the olefinic region rather difficult. As discussed in Section III-A, a similar problem has been encountered in many of the monohaptocyclopentadienyl complexes of the transition metals. There is considerable evidence to suggest the olefinic protons closest to the metal (H1,4) will resonate at lower fields in such compounds. On this basis the multiplet at 6.64 ppm is assigned to H1.*

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*The designation of one of the H1/H4 resonances is of course arbitrary.

Once the choice of H1 has been made, the other olefinic signals can be assigned by decoupling experiments. Decoupling of H1 resulted in loss of a large coupling to the peak at 6.08 ppm. As the only large couplings in the η^1-C_5H_5 ring should be across the double bonds,[150] the peak at 6.08 ppm is assigned to H2. The other resonance at 6.30 and 6.16 ppm have a coupling similar to that of J(H1-H2) and are assigned to H4 and H3. At this point a choice between H4 and H3 cannot be made.

The spin saturation transfer method was used to determine the path of metal migration in (η-C_5H_5)Re(CO)(NO)-(5-η^1-C_5H_5) ($\underset{\sim}{23}$). The intensity loss on irradiation was measured by integration *versus* the η-C_5H_5 peak. Saturation of H5, the aliphatic proton, resulted in an intensity loss at the 6.64 and 6.30 ppm signals (Figure XIIIb). On the basis that the peak at 6.64 ppm is H1, the shift pathway would be 1,2. This experiment also enables assignment of the peak at 6.30 ppm to H4. The remaining signal at 6.16 ppm must therefore be H3.

The choice of 1,2 shifts as the path of metal migration for (η-C_5H_5)Re(CO)(NO)(5-η^1-C_5H_5) is of course dependent upon the correct assignment of the olefinic protons. Other metal systems in which a 1,2 pathway has been inferred suffer from the same limitation. However, in the case of the rhenium compound there is important further evidence for the correct assignment of the ^1H NMR spectrum. Throughout the present study it has been noted that the chemical shift difference between diastereotopic proton (or carbon) pairs increases with proximity to the metal. This trend can be maintained with $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ only if the ^1H NMR spectrum of Figure XIII is assigned as discussed above. The chemical shift difference between H1,H4 is greater than between H2,H3. This observation suggests that the correct assignment and therefore the correct pathway for metal migration has been chosen.

To determine the stereochemistry of the 1,2 shifts in $\underset{\sim}{23}$, it is necessary to saturate one of the protons in the olefinic region. For this purpose H1 was chosen. Saturation at H1 should result in an intensity decrease at H5 and H2 if the 1,2 shift occurs with *retention*, or at H5 and H3 if metal migration occurs with *inversion* of configuration at the metal. As shown in Figure XIIIc saturation of H1 resulted in a decrease in intensity of the peaks at 4.90 and 6.08 ppm. As these positions are assigned to H5 and H2, 1,2 shifts must be occurring with *retention* of configuration at the metal center.

An experiment similar to the one discussed above was carried out by Mann and co-workers.[159] Metal migration in $(\eta\text{-}C_5H_5)(ON)[(S_2CN(n\text{-}Bu)_2]Mo(5\text{-}\eta^1\text{-}C_5H_5)$ was shown to occur *via* a 1,2 shift. It was not specifically discussed in the paper, but Mann's results are also consistent with retention of configuration at the metal during sigmatropic shifts. The conclusions concerning the path of migration in the molybdenum compound are also dependent upon the correct assignment of the olefin positions.

The experiments performed with $(\eta\text{-}C_5H_5)Re(CO)(NO)\text{-}(5\text{-}\eta^1\text{-}C_5H_5)$ demonstrate a further example of 1,2 shifts in monohaptocyclopentadienyl complexes of the transition metals. The presence of the chiral metal center in this compound has provided a convenient method for determining both the pathway and stereochemistry of metal migration. In the rhenium system 1,2 shifts occur with retention of configuration at the metal. These results are in accord with the predictions of orbital symmetry rules as applied to sigmatropic shifts.

SECTION V

EXPERIMENTAL

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_8)$ (22).

Triethylamine (0.20 mL, 1.44 mmol) was added dropwise to a solution of $(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_7H_7)BF_4$ (0.50 g, 1.02 mmol) in 10 mL of CH_2Cl_2. The solvent was removed under reduced pressure to give a red solid. This solid was extracted with hexane, filtered, and cooled to -20°C to give red crystals of the monohaptocycloheptatrienyl compound 22, 0.37 g, 90% yield, MP 94-95°C.

Characterization: IR (hexane) 1967(s), ν(CO); 1712(s) cm^{-1}, ν(NO). Mass Spectrum, 70°C/12 ev: $[CpRe(CO)(NO)C_7H_7]^+$, $[CpRe(NO)C_7H_7]^+$, $[CpReC_7H_7]^+$. Proton and carbon NMR (see discussion). Anal. Calcd for $C_{13}H_{12}ReO_2N$: C, 38.99; H, 3.02; N, 3.50. Found: C, 38.89; H, 3.02; N, 3.68.

Preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ (23).

(a) From $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (9).

$(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ (0.55 g, 1.41 mmol) was dissolved in 15 mL of THF and cooled to -15°C. A solution of NaC_5H_5 in THF was added dropwise, until infrared monitoring indicated all the bromide had been consumed. The dark red solution was warmed to room temperature and the solvent removed under reduced pressure to give a black, tarry residue. The residue was extracted with hexane, filtered and cooled to -78°C giving a red solid. Recrystallization from hexane at -20°C gave the monohaptocyclopentadienyl compound $\utilde{23}$ as red crystals, 0.20 g, 42% yield. Characterization: IR (hexane) 1972(s), ν(CO); 1720(s) cm^{-1}, ν(NO). Mass Spectrum, 35°C/14 ev: $[CpRe(CO)(NO)C_5H_5]^+$, $[CpRe(NO)C_5H_5]^+$, $[CpReC_5H_5]^+$. Proton and carbon NMR (see Discussion). Anal. Calcd for $C_{11}H_{10}ReO_2N$: C, 35.28; H, 2.69; N, 3.74. Found: C, 35.25; H, 2.71; N, 3.91.

(b) From $[(\eta-C_5H_5)Re(CO)(NO)(THF)]PF_6$ ($\utilde{11}$):

$[(\eta-C_5H_5)Re(CO)(NO)(THF)]PF_6$ (0.23 g, 0.44 mmol) was suspended in 10 mL of THF and cooled to -20°C. A solution of NaC_5H_5 in THF was added dropwise until all the starting material had dissolved. The dark red solution was warmed to room temperature and the solvent removed under reduced pressure to give a black, tarry residue. The residue was extracted with hexane, filtered, and cooled to -78°C to give a red solid. The compound was crystallized from hexane at -20°C, 0.042 g, 26% yield. The monohaptocyclopentadienyl compound $\utilde{23}$ was identified by comparison of its infrared, proton NMR, and mass spectra to authentic samples.

Reactions of $(\eta\text{-}C_5H_5)Re(CO)(NO)(\eta^1\text{-}C_7H_7)$ (22).

(a) Protonation with HBF_4/Et_2O:

$(\eta\text{-}C_5H_5)Re(CO)(NO)(7\text{-}\eta^1\text{-}C_7H_7)$ (0.10 g, 0.25 mmol) was dissolved in 10 mL of diethyl ether at room temperature giving a red solution. The addition of HBF_4/Et_2O gave a yellow solution from which quickly precipitated a yellow solid. The solid was collected, washed with 3 x 10 mL of ether and dried *in vacuo*, 0.114 g, 94% yield. Infrared and proton NMR spectroscopy showed this material to be the cycloheptatriene cation 18.

(b) Protonation with anhydrous HCl:

$(\eta\text{-}C_5H_5)Re(CO)(NO)(\eta^1\text{-}C_7H_7)$ (0.10 g, 0.25 mmol) was dissolved in 5 mL of CH_2Cl_2 at room temperature to give a red solution. Hydrogen chloride was bubbled through the solution for ~15 sec, resulting in a bright yellow color. Infrared monitoring at this point suggested the presence of the cycloheptatriene cation 18. The solution was stirred for 1 hr during which the color changed from yellow to dark red. The solvent was removed under reduced pressure to give a red solid which was washed with 3 x 5 mL of hexane. Comparison of the spectroscopic properties of this material with those of $(\eta\text{-}C_5H_5)Re(CO)(NO)Br$ suggests the product was $(\eta\text{-}C_5H_5)Re(CO)(NO)Cl$, 0.067 g, 78% yield.

Characterization: IR (hexane) 2004(s), ν(CO); 1744(s), ν(NO). Mass Spectrum, 100°C/14 ev: $[CpRe(CO)(NO)Cl]^+$, $[CpRe(NO)Cl]^+$. Proton NMR (CD_2Cl_2) δ5.85 ppm.

(c) Protonation with Trifluoroacetic acid;
preparation of $(\eta\text{-}C_5H_5)Re(CO)(NO)O(O)CCF_3$:

$(\eta\text{-}C_5H_5)Re(CO)(NO)(\eta^1\text{-}C_7H_7)$ (0.10 g, 0.25 mmol) was dissolved in 5 mL of CH_2Cl_2 at room temperature giving a red solution. Trifluoroacetic acid (0.037 mL, 0.50 mol) was added dropwise to give initially a yellow solution which became orange after stirring for 0.5 hr. The solvent was removed under reduced pressure to give an orange solid. The solid was extracted with diethyl ether, filtered and cooled to -78°C to give orange crystals of the trifluoroacetate ester 26, 0.085 g, 81% yield, MP 134-135°C.

Characterization: IR (hexane) 2015(s), 2004(m), ν(CO); 1754(m), 1746(s), ν(NO); 1716(m) cm^{-1}, ν(CF_3COO) (see Discussion). Mass Spectrum, 95°C/16ev: $[CpRe(CO)(NO)O(O)\text{-}CCF_3]^+$, $[CpRe(NO)O(O)CCF_3]^+$. Proton NMR (CD_2Cl_2) δ5.90 ppm. Anal. Calcd for $C_8H_5ReO_4NF_3$: C, 22.75; H, 1.19; N, 3.32. Found: C, 22.63; H, 1.44; N, 3.38.

Protonation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ with HBF_4^-.

$(\eta\text{-}C_5H_5)Re(CO)(NO)(5\text{-}\eta^1\text{-}C_5H_5)$ (0.10 g, 0.27 mmol) was dissolved in 10 mL of diethyl ether at room temperature giving a red solution. The addition of HBF_4/Et_2O gave a yellow solution from which quickly precipitated a yellow solid. The solid was washed with 3 x 10 mL of ether and dried *in vacuo* to give $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$ 0.12 g, 97% yield.

Characterization: IR (CH_2Cl_2) 2053(br,s), ν(CO); 1779.0(s) cm^{-1}, ν(NO). Proton NMR (see Discussion). Anal. Calcd for $C_{11}H_{11}ReO_2NBF_4$: C, 28.58; H, 2.40; N, 3.03. Found: C, 28.40; H, 2.38; N, 3.02.

Deprotonation of $(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)BF_4$.

Triethylamine (0.10 mL, 0.72 mmol) was added dropwise to a solution of $[(\eta\text{-}C_5H_5)Re(CO)(NO)(1,2\text{-}\eta^2\text{-}C_5H_6)]BF_4$ (0.10 g, 0.22 mmol) in 10 mL of CH_2Cl_2. The solvent was removed under reduced pressure to give a red solid. This solid was extracted with hexane, the solution filtered and cooled to -40°C to give red crystals of the monohaptocyclopentadienyl compound 23, 0.074 g, 91% yield. The product was identified by comparison of its IR, ^1H NMR and Mass Spectrum to authentic samples.

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